Textile Conservation: Deterioration of Materials

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ROCHESTER INSTITUTE OF TECHNOLOGY
TEXTILE CONSERVATION
DETERIORATION OF MATERIALS
A THESIS SUBMITTED TO
THE FACULTY OF THE COLLEGE OF FINE
AND APPLIED ARTS
DEPARTMENT OF TEXTILES
BY
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Preface

In preparing this text I found myself faced with what initially appeared to be an insurmountable challenge: to locate and organize all the attitudes, opinions, and methods of textile conservators, most of which is spoken word or scattered in various, obscure places. Furthermore, the potentiality of scientific research in the natural resources enterprises is neither generally recognized nor appreciated. The textile industry comprises one of the oldest and largest areas of natural resource enterprise...Considering the fact that the beginnings of textiles can be traced back some hundreds of thousands of years, the evolution of this great and important unit of the three fundamental needs of man is worthy of serious contemplation. 1

Complete coverage of the information long over-due to textile conservation, would realistically take years. In consideration of these facts, I have placed limitations upon my research and artistic works as they directly relate to my participation in the Master of Fine Arts Textile Program at Rochester Institute of Technology.

Having acquired several archaic textiles, I felt an obligation to preserve them as historical documents and to maintain their present condition for future pleasure and reference. Thus, I began an investigation of the deterioration of materials and conservation of textiles. Personal acknowledgment of using process as an art form, has enriched my textile structures and suggested, ultimately, the body of my thesis studio work: a presentation of deteriorated or ruinous states of textile structures as an aesthetic statement.

I wish to acknowledge Mr. Donald Bujnowski, my chief advisor, for his progressive attitudes, facile shop stamina, wealth of information, and determination to support my endeavors; Mr. Max Lenderman, an undying source of energy and accumulated data; and Mr. Robert Heischman, for absorbing and understanding the potential of my ideas in their elementary stages and...

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It is difficult to acknowledge an inanimate environment. However,
Rochester Institute of Technology, its facilities and resources, are very
much alive and fundamental to the mechanics of my thesis. The Marriott
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Introduction

Ethics and Aesthetics of the Preservation of Historic and Artistic Works

Textile conservation is a relatively new field. Only in the last twenty-five years have museums begun to research the preservation of textile specimens. There is some disagreement over which methods are best, and which are most harmful. No one museum curator, or conservator, has the last word on the subject. Each institution has its own theories and techniques in caring for its collection. Even the most basic rules of conservation are subject to question and revision. It is quite possible that in a decade new scientific techniques and substances will make methods of preservation obsolete.

No two museum textile specimens are exactly alike. The fiber content, dyes, construction, past treatment and storage combine to give each specimen a unique set of conservation needs and problems. Although there are some general rules and guidelines that can be amended to accommodate the special needs of the object and the limitations of the institution holding it. ¹

The preservation of physical evidence of textile history to increase the knowledge and understanding of the development of various technologies is important. It is more than collecting historic memorabilia or examples of decorative arts. In the effort to conserve these materials it is important that the purpose for which the textile is being preserved is not destroyed. Destruction can result from an overzealous attempt to make a textile look good or as new. A conservative attitude is the very substance of conservation. With a conservator, the decision must be made as to the best method of continually conserving the textiles collected. Detailed analyses are made to identify, understand, and verify the textile selected. Equally important, detailed records must be kept of any work done in the conservation. ²

Having surveyed current opinions regarding the preservation of textiles, it appears that, on the whole, the conservative attitude is still dominant over the so-called progressive attitude. The conservative approach advocates the use of natural materials for sewing yarns and supporting fabrics (silk, cotton, and linen) and natural methods of bleaching (sunlight, moonlight, grass-bleach). The progressive approach is not opposed to the application of yarns and fabrics consisting of man-made fibers (rayons, polyamides, such as Nylon 66, Nylon 6, polyesters, such as Dacron and Terylene, and polyacrylonitriles, such as Dralon and Orlon) or synthetic adhesives, such as polyvinyl alcohol, polyvinyl acetate and its co-polymers, and polymethacrylates. 3

Whichever approach is favored, it is evident that in the preservation of culturally important textiles, one has to avoid those methods which affect the appearance and the touch of the objects unfavorably, if a better alternative exists. Sometimes the best method will be to do nothing, especially in those cases where the fabrics are greatly weakened, and their aesthetic value is much greater than their historic value. In a few cases, even the removal of dust by soft brushing or by careful rinsing in water will be sufficient. More often a mild washing in a solution of a detergent will give the desired results. However, when the objects are very damaged/weakened, one of the reinforcing methods may be applied. Decision for selecting the proper techniques is difficult, because, in principle, every method has its advantages and disadvantages.

The method which has been accepted by prominent art historians is the sewing of the object on or between transparent silk fabrics. The aesthetic effect may be improved by using fabrics dyed in a matching color. When this method is used, the appearance as well as the touch are more or less adversely affected, but the textile character of the object has been preserved. In cases where this sewing technique would not be appropriate or applicable, and the object still merits preservation, then methods of reinforcement by impregnation with resins and/or adhesion to thin, transparent support fabrics may be tried. Here, it is not only the appearance and the touch which are affected, but depending on the chosen chemicals and on their concentrations, the flexibility of the structure may also be altered. The change in the latter property may lie between nearly imperceptible and totally unacceptable. The conservator will also have to consider: the reversibility of the alternative treatments, assessing

possible accelerating effects of the added fabrics and chemicals on the
deterioration of the object, as well as the preserving properties of some
of the recommended chemicals. It is clear that these decisions must not
be made by intuition, but must be accountable to scientific arguments.

Even when the best method for the given circumstances has been
determined, by considering material, climate, capability of the restorer,
and then applied, the restored object is still liable to deterioration.
All the care, energy and money spent on conserving textile specimens will
have been wasted if they are not going to be kept in the right preserving
environment. 4

It is probably true that textile-mending has been carried out for
nearly as long as textiles have been used by man. Mending of holes
and tears in garments and other textiles is more or less comparable
with what is generally understood by restoration of textiles. It is
only when the textiles, in the course of time, have acquired artistic
or historic value, that it is necessary to make high demands upon the
manner in which the mending has to be carried out. 5

This, however, should not lead to the conclusion that every valuable
textile which has been damaged by some cause should be mended. The
conviction that the style and the character of the object concerned must
be preserved is fundamental. Two divergent opinions have evolved from this
premise and should be recognized.

The first opinion is that if mending has to be done at all, it should
be as invisible as possible. It is carried out on the condition that all
repairs are documented by photographs and detailed reports. This method
may mean reweaving tapestries, knotting a new pile in rugs or darning
according to design in other fabrics. There remains, of course, a certain
degree of insincerity towards the unsuspecting visitor, who finds himself
confronted with a textile object, of which absolute authenticity is
suggested, because there is no mention of restoration. This objection,
however, can be partly removed by providing schematic drawings or
photographs which delineate the restored parts of the object.

The second opinion is that honesty, with regard to the observer and
with respect to the artist who created the textile, requires that the
repairs have to be carried out in a manner whereby mended parts can easily

5 Johan Lodewijks and Jentina E. Leene, "Restoration and Conservation,"
in Textile Conservation, ed. Jentina E. Leene (London: Butterworths,
be distinguished from the authentic, without disturbing too much the effect of the original work of art. This can be attained, for example, by sewing fabrics with structure and color slightly different from the authentic object behind the holes and tears. In other words, all possible measures should be taken to preserve what has been left at the moment of conservation and to avoid further deterioration. This opinion has gained much support.

To summarize, then, there are two important groups of preservation methods:
1. Restoration methods which, in principle, are directed towards restoring the original state, and
2. Conservation methods which aim at preserving the 'status quo'.

The choice between restoration and conservation depends on different rational factors, apart from irrational ones such as aesthetic and other feelings. When a textile has a representative function, one is more apt to decide on restoration. In museum collections items do not generally have a representative function and conservation methods should be considered very carefully. 6

Textile conservation, as presented in this thesis, is defined as: the preservation of the 'status quo' of a given or specific item: slowing the deterioration of its components from that point onward.

The quotation of authorities is appropriate in the first three chapters of this thesis as my interest in process as an art form requires correct and scientific research: both past and present theories. The information researched has been absorbed; my values and conclusion coincide with what has been cited. The detailed descriptions are perhaps tedious to the untrained individual but essential in enriching my studio art work.

6Ibid., pp. 137-138.
CHAPTER I

PROPERTIES OF MATERIALS I USE

Before beginning conservation treatment on any textile the first step is to carry out an examination with a pocket lens or binocular microscope on that structure and to make a record of the following physical and visual characteristics of its fibers, yarns, and fabric.

1. The nature of the fibers of both warp and weft threads
2. Spun threads - the direction of the twist S or Z
3. The type of weave - tabby, twill, figured
4. Count per inch of both warp and weft threads
5. The presence of selvages
6. Applied decoration: gold-leaf, metal threads, embroidery
7. The presence of sewing thread or stitch holes
8. The condition: mechanical, chemical or biological damage
9. The presence of colorants: dyes, lakes, stains, paints, or soils

If the material is very dirty, making analysis difficult, gentle blasts of air from a blow-ball or bellows may be used to remove loose dust, or in some cases a soft brush may be used. It may be impossible to record all particulars until the textiles have been washed, but it is important to get as much information as possible in the first place in case any evidence should be lost during treatment. ¹

Fiber Structure

Fiber structure includes the external structure, the internal structure, and the chemical composition.

External Structure

Length: 1. Filaments are long continuous strands. Silk is the only natural filament fiber. Yarns made from filament are of two types: monofilament and multifilament. Monofilament yarns are made of a single fiber of high

strength and smoothness. Multifilament yarns are made of a number of tiny filaments with or without twist. The size and number of the filaments may vary.

2. Staple Fibers: either natural or man-made, are short in length and are measured in inches. They range from ½ inch to 24 inches in length. All the natural fibers except silk are staple.

**Diameter**

The finer the diameter of a fiber, the more pliable it is and the softer it feels. The thicker the fiber, the more body and stiffness it has and the more it will resist crushing. In natural fibers, fineness is a major factor in determining quality. Fineness is measured in microns (1/1000 of a millimeter).

**Cross Sectional Shape**

Shape is important in luster, bulk, and body and helps determine the hand or feel of the fabric. The natural fibers derive their shape from the way (1) the cellulose is built up during the plant growth; or (2) the shape of the orifice through which the silk fiber is extruded; or (3) the shape of the hair follicle and the formation of protein substances in animals.

**Surface Contour**

Surface contour may be smooth, serrated, lobular, or rough. The surface contour is defined as the surface of the fiber along its shaft.

**Crimp**

Crimp refers to the waves, bends, or twists that occur along the length of the fiber. Fiber crimp should not be confused with weave crimp, which results from the interlacing of yarns in the fabric, nor with molecular crimp, which results from the way molecular chains are built up. Fiber crimp increases cohesiveness, resiliency, resistance to abrasion, and gives increased bulk and warmth to fabrics. It helps fabrics to maintain their loft or thickness, increases absorbency and skin-contact comfort, but reduces luster. A fiber may have one of three kinds of crimp: mechanical crimp, natural or inherent crimp, or latent (chemical) crimp. Mechanical crimp is imparted to fibers by passing them through fluted rollers to produce a two-dimensional, sawtooth crimp. The bends are angular in contrast to the rounded waves of a natural crimp. Natural or inherent crimp occurs in cotton and wool. Cotton has a two-dimensional twist call convolutions. Wool has a three-dimensional crimp. Latent or chemical crimp exists in the fiber in an undeveloped state until the
finished garment is either (1) immersed in a suitable solvent, or (2) given a heat treatment to develop the crimp. This kind of crimp occurs in fibers that have been modified in the spinning solution or in the extrusion process. The modification produces a fiber that will shrink more on one side than it does on the other. High shrinkage of one side forces the fiber to curl.

Distinctive Parts
The natural fibers, except for silk, usually have three distinctive parts: an outer covering called a skin or cuticle, an inner area, and a central core that may be hollow.

Internal Structure
The internal structure of fibers is described in these terms:

Degree of Polymerization
Fibers are composed of millions of molecular chains held together by cross links or molecular bonds. The length of the chains vary just as the length of fibers vary. The chain length is described as degree of polymerization (D.P.). Polymerization is the process of joining molecules together and if many molecules are joined together to make a chain, the fiber has a high degree of polymerization.

Cross Links
Molecular chains are held together by cross links or bridges between the chains or by attractive forces called hydrogen bonds and Van der Waals forces.

Amorphous
Hydrogen bonding is the attraction of hydrogen atoms (which have a positive force) of one chain and oxygen or nitrogen atoms (which have a negative force) of an adjacent chain. The closer the chains are together, the stronger the bonds. Van der Waals forces are similar but weaker bonds. Molecular chains lie in various configurations in the fiber. Molecular chains in a random or unoriented arrangement is called amorphous.

Oriented
Molecular chains in an orderly arrangement.

Crystalline
Areas in a fiber in which the molecular chains are parallel to each other and close together. It is in the crystalline areas that hydrogen bonding and Van der Waals forces occur.
Chemical Composition

The chemical composition of fibers is the factor that makes one fiber family (generic group) different from another. It is the basis for classifying fibers as cellulose, protein, acrylic, and so on.

Fiber Properties

Properties are characteristics by which one kind of matter may be distinguished from or compared with other kinds of matter. Fiber properties are due to the structure of the fiber.

Abrasion resistance
the ability of a fiber to withstand the rubbing or abrasion it gets in everyday use.

Absorbency (Hydrophobic, hygroscopic)
the ability of a fiber to take up moisture and is expressed in terms of moisture regain, which is the percentage of moisture that a bone-dry fiber will absorb from the air under standard conditions of temperature and moisture.

Chemical reactivity
the effect of acids, alkali, oxidizing agents, solvents.

Cover
the ability to occupy space for the purpose of concealment or protection due to crimp, curl, or twist and cross-sectional shape.

Cohesiveness
the ability of fibers to cling together during spinning. This is an important property in staple but not in filament.

Creep
delayed elasticity, the fiber does not recover immediately from strain but will recover gradually.

Density (Specific Gravity)
measures of the weight of a fiber. Density is the weight in grams per cubic centimeter, and specific gravity is the ratio of the mass of the fiber to an equal volume of water at 4° Centigrade.

Dyeability
the ability of fibers to accept dyes.

Elastic recovery
the ability of fibers to recover from strain.

Elasticity
the ability of a stretched material to return immediately to its original
size.

**Electrical conductivity**
the ability to transfer electrical charges, a good conductor does not build up static electricity.

**Elongation**
the ability to be stretched, extended, or lengthened. For production of yarns and fabrics a minimum of 10 percent elongation is desirable. 
Elongations vary at different temperatures and when wet or dry.

**Flammability**
the ability to ignite and burn.

**Hand**
the way a fiber feels when handled - silky, harsh, soft, crisp, dry.

**Heat conductivity**
the ability to conduct heat away from the body.

**Heat sensitivity**
the ability to soften, melt, or shrink when subjected to heat.

**Luster**
the light reflected from surface. It differs from shine in that it is more subdued, since the light rays striking the surface are broken up.

**Loft**
compressional resiliency, the ability of a fiber, yarn, or fabric to spring back to its original thickness after being compressed. In fibers loft is due to crimp.

**Pilling**
the balling up of fiber ends on the surface of fabrics.

**Resiliency**
the ability of a fiber or fabric to recover over a period of time from deformations of stretching, bending, or twisting.

**Stability**
retention of size, shape, or form.

**Stiffness**
rigidity is the opposite of flexibility. It is the resistance to bending or creasing.

**Strength**
of a fiber is defined as the ability to resist stress and is expressed as tensile strength (pounds per square inch) or as tenacity.
Sunlight resistance

the ability to withstand degradation from direct sunlight. ²

Cotton

History

The origin of cotton is older than any recorded history. Probably this fiber originated in India. Ruins of cities in the Indus Valley show that cotton was grown and used there as early as 3000 B.C. Recorded history tells us that cotton was being woven into cloth as early as 1500 B.C. The spread of the production of cotton and its manufacture into cloth is unrecorded, but the cloth and the art of its weaving found their way into Persia, Egypt, and other markets during very early times. Mummies wrapped in fine cotton cloth have been found in Peruvian ruins which date as early as 8,000 B.C. ³ Although cotton was grown in Asia Minor early in the Christian Era, it was not grown in Europe until its introduction into Spain by the Moors in the tenth century. The name cotton is derived from an early Arab word Quttan or Kuru means a plant found in conquered lands. The other European countries continued to import cotton from Asia until the Mohammedan conquest of Constantinopile closed the trade routes between Europe and the East. Cotton was one of the causes for the growth of the great market cities of the Middle Ages, such as Venice and Genoa.

Columbus sailed westward and Vasco da Gama sailed eastward; both with intentions to open new routes to India. Through his expedition, Columbus found cotton growing in the Bahama Islands in 1492.

Of all the textile fibers in use, cotton, in addition to being the most important economically, is the shortest; the most deformed as far as any regular appearance is concerned; the most variable in size within the structure of a single fiber; the most uneven in maturity and uniformity; the most demanding in terms of the various handling and processing techniques between fiber and finished fabric; as well as being one of the


³"Thanks to the techniques of modern archaeology and probably to a more optimistic approach in looking for texture remains, we now have actual fragments from at least 8,000 B.C. in the New World and about 6,500 B.C. in the Old World." Mary Elizabeth King, "Archaeological Textiles", in Archaeological Textiles: Irene Emery Roundtable on Museum Textiles, 1974 Proceedings, ed. Patricia L. Fiske (Washington, D.C., The Textile Museum, 1975), p. 9.
most versatile of all fibers in its end-use applications after the fabric is finished. Literally thousands of individuals have devoted their knowledge, imagination, and labor to the perfection of cotton textiles as documented in prehistoric fabric remnants, historical references, and as evidence in our present times.

The real growth of cotton came with the introduction of machinery. This lowered the cost of processing cotton goods. Not only the economics but the politics of great nations were affected by the changing condition of the cotton trade.

The names of seven inventors, six Englishmen and one American, stand out among the many geniuses who contributed to this industrial revolution which mechanized the processing of cotton and other fibers. John Kay was trained in textiles by his father, a woolen manufacturer. It was his flying shuttle, invented in 1730, which enabled English weavers to make cotton as wide as the fabrics from India. Mechanization was to the hand workers of his day, when cotton was practically outlawed in England, much more of a threat than automation is today to our industrial workers. The first bobbin machine was destroyed by mobs.

James Hargreaves, a cottage weaver, made in 1764, the first practical spinning frame, which was called the Spinning Jenny. It could manipulate eight spindles at one time. Hargreaves finally developed one which could operate 100 spindles.

Richard Arkwright, a barber, conceived the roller-spinning method in 1771. Within two years, the first cotton mill was to use his roller-spinning method. The first power to be used was actually horsepower, the movement of a treadmill being utilized. This spinning frame successfully drew raw stock into a finished spun yarn. Water power as a source of energy was soon used in England by Arkwright's machines.

Samuel Slater worked as a machinist in an Arkwright mill before coming to America. Though Slater did not assume the stature of these other inventors, he brought in his memory a complete working plan for the Arkwright power spinner and became, himself, one of the largest builders of cotton processing machinery in the United States at about the beginning of the 19th century.

Samuel Crompton was described as a musician and mechanic as well as a dreamer. In 1779, his spinning mule perfected the art of spinning fine cotton yarns, and, indeed, it is the principle on which much of today's
textile spinning depends. He personally realized less from his invention than did any of his compatriot geniuses. Edmund Cartwright was educated to be a clergyman but became an inventor. In 1785, he gave the textile world its first automatic powered loom. Like the other inventions, Cartwright's depended a good deal upon the work of his predecessors; but there is a vast difference between inventive ideas which do not work and that one which is peristently improved until it does perform efficiently.

Eli Whitney, a young Yale graduate visiting in the South, found that the easy life of his well-to-do Southern friends appealed to him. His inventive ability was challenged by the complaints of his friends of the time, labor, and expense involved in removing the cotton fibers from the seed. In 1792, Whitney's cotton engine, or gin, was completed, operated by means of a hand crank; a mass of raw cotton was plucked at and torn apart by small sawteeth, which carried away the linters and allowed the seeds to drop.

Cotton became "King of the South"; in the northern states there was an abundance of water power and textile mills grew rapidly in number. The spread of textile mills in southern states grew slower but today about 80 percent of our textile industry is south of the Mason-Dixon Line. 4

Types of Commercial Cotton

Cotton is the white or yellow-white fiber covering the seeds of a species of plant of the botanical classification gossypium. The plant belongs to the natural order of the MALVACEAE, or the mallow family. There are various species; Gossypium herbaceum and Gossypium hirsutum are mainly cultivated in America and India. Gossypium peruvianum, as its name implies, originated in Peru and spread to other South American countries and Gossypium barbadense produces the fine silky Sea Island cotton. Sea Island

The fibers of this species are about 1.6 inches in length and may be as long as two inches if the soil is good and the cultivation has been carefully maintained. This cotton is raised on the islands off the coast of the Carolinas and along the coast of the southern states. At present, its production in the United States is small because of inroads of the boll weavil in the areas favorable to the growth of this cotton. Because

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of the fineness of the fibers and their length and uniformity, this species is highly prized for laces and fine weaving yarns from 120's to 200's count.

**Egyptian**

This species is next to the Sea Island in fineness and fiber length. The average length is between 1.5 and 1.75 inches. It is grown along the delta of the Nile River. These fibers are brownish in color.

**Peruvian**

The Peruvian species of cotton is found in Central and South America and the West Indies. Some types are moderately smooth. The characteristic fiber is rough and wiry and approximately 1 to 1.5 inches in length. The rough Peruvian fiber is a tree cotton producing two crops a year.

**American**

The bulk of the domestic United States cotton produced for world consumption is of the genus Hirsutum. There are three main types of American cotton, classified geographically into Gulf, Texas, and Upland cotton. The staple varies between 1 and 1.25 inches, Gulf cotton is the product of the states bordering the Gulf of Mexico. It is generally regarded as one of the better of the American types. The color is almost pure white, and the fiber length is about one inch.

Oklahoma- and Texas-grown cotton is classified as Texas. The fibers are slightly shorter than the Gulf type, and they are harsher. To a large extent Pima cotton has replaced the shorter Texas fiber.

Upland cotton, the major cotton fiber grown in the United States, is produced on the plantations of Georgia, Alabama, Tennessee, Virginia, and the Carolinas. Some varieties grown in Arkansas, Mississippi, and Louisiana are classified as Upland Cotton. This type has an average fiber length of 15/16 of an inch.

**Pima cotton** developed by the United States Department of Agriculture, is the finest long-staple cotton of commercial importance in the United States. It is grown under irrigation conditions in the southwestern part of the United States, Arizona, the Texas Panhandle, New Mexico, and California. The fiber length is generally about 1.0 inch to 1.25 inches.

**Indian cotton** This is a short fiber between 0.6 and 0.8 inches in length. It is therefore only suitable for spinning coarse counts.

**China cotton** This is about the lowest commercially-acceptable grade, the fibers being only 0.5 to 0.7 inches long. Its twist is not highly developed and it is rather harsh. It does not spin a good yarn alone, and is usually
used in a mixture with better qualities.  

Classification of Cotton

The significance of staple length in spinning cannot be over-emphasized, because the quality of the yarn produced will be greatly reduced if a shorter fiber than customary is used. A practical grading according to staple length is as follows:

2. **Short staple** - between 13/16 and 15/16 of an inch.
3. **Medium staple** - between 15/16 and 1 1/8 inches. This length includes most of the American cotton and is the usual American Upland staple.
4. **Extra-long staple** - from 1 3/8 to 2 1/2 inches long. The lustrous cottons from Egypt and our limited supply of Sea Island cottons belong to this group.

The quality of cotton is affected by color and brightness, the amount of immature cotton fibers which may be mixed in, the amount of foreign material, and, in general, the quality of the ginning operation. For these grades, the United States Government has set the standards. These grades are as follows, with the highest grade given first and the others in descending order:

1. Middling-fair
2. Strict good-middling
3. Good middling
4. Strict middling
5. Middling
6. Strict low middling
7. Low middling
8. Strict good ordinary
9. Good ordinary
10. Ordinary

Since these are white cotton, the degree of whiteness also enters into the rating in a sub classification. These are extra-white, white, spotted, tinged, yellow, stained, and grey.

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The last term, character, refers to the strength, maturity, uniformity, and smoothness of the fibers, and to other qualities which are not covered by staple length and grade. Regardless of the grade, uniformity is a prime requisite if the best use is to be made of the cotton.  

Cotton Spinning

The twisting process by which fibers are formed into a yarn is referred to as spinning. In the cotton textile industry, however, spinning includes all the processes required to prepare and clean the fibers, from the opening of the bale to the twisting of the yarn in its preparation for the textile loom. As the mass of cotton fiber is successively cleaned and formed into ever narrower and more compact configurations, it is identified by different terms. Thus, the term lap refers to the broad loose mass of cotton fibers as laid down after the cleaning and picking operation. Sliver refers to the somewhat narrower layer of cotton into which the fibers have been combed and lie more parallel. Roving is a thinner strand formed by loosely twisting the paralleled cotton fibers into a rope-form. Yarn is the fine, more tightly twisted strand produced by further drawing and twisting of the roving until the proper size and tightness have been reached for use in the weaving operation.

Classification of Yarns

The classification of yarns is based upon thickness; another way of expressing it would be in terms of the relative fineness. By this method, numbers are assigned to express the fineness of the yarn, the number being of hanks or strands of cotton, 840 yards long, required to weigh one pound; thus, if we have a hank of yarn 840 yards of which weigh one pound, we would call this a number 1 or 1's cotton. Five's cotton would be 1/5 the diameter or thickness of 1's, because it would take five of these hanks, or a total of 4200 yards, to weigh one pound. If these are single yarns, the designations for 5's, 10's, or 20's are respectively 5/1, 10/1, and 20/1. If these are two-ply yarns of the same size the number of the ply would appear below the slash as follows: 5/2, 10/2, 20/2. In the case of ply yarns, however, the size or classification depends upon the number of plies as well as the fineness of the individual yarns making up the ply.

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6 Labarthe, Textiles: Origins to Usage, pp. 131-32.
7 Ibid., pp. 133-41.
Each cotton fiber is a unicellular hair collected from the seed of the cotton plant. The function of these hairs is to protect the young unripe seed and to assist in its dispersal when it is mature. Each fiber, however long or short it may be, consists of one single complete vegetable cell. A fundamental difference between animal and vegetable cells is that the former have no protective wall while the latter have an outer skin composed of cellulose. Enclosed within this wall is the living protoplasm and a fluid which is essentially a solution of various mineral salts, called cell sap. Protoplasm is a jelly-like substance of very complex chemical constitution composed of nitrogenous substances called proteins. In a young and growing cell the whole of the enclosed space is filled with protoplasm and cell sap so that the structure is distended and turgid.

When the cell becomes mature the protoplasm dies and the sap disappears, leaving an almost empty structure. The cotton fiber is now dead and the contents of the cell are no longer visible under the microscope, but the dried-up protein and the salts which are deposited as the sap evaporates still remain in the central cavity. These are among the impurities which have to be removed when the cotton is scoured and bleached. ⁸

The cotton fiber is made up of a cuticle, primary wall, secondary wall, and a lumen.

The cuticle is a wax-like film covering the primary or outer wall. The secondary wall contains successive layers of cellulose similar to the growth rings of a tree. One layer is laid down each day of the 20 to 30 days of growth. Each layer is built up of fibrils - bundles of molecular chains - which are laid down in a spiral arrangement. At intervals, the spirals reverse direction. These reversals of spirals are an important factor in the twist, elastic recovery, and elongation of the fiber, as well as in yarn strength.

The lumen is the central canal through which the nourishment travels during growth. In the mature fiber, the dried nutrients in the lumen give the characteristic dark areas that can be seen under a microscope.

Convolutions or ribbon-like twists characterize the cotton fibers.

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⁸ Trotman, Dyeing and Chemical Technology of Textile Fibres, Third ed., p. 33.
As the fiber matures, the lumen collapses and the reverse spirals cause the fiber to twist. The twist forms a natural crimp that enables the fibers to cohere to one another, so that despite its short length, cotton is one of our most spinnable fibers. Convolutions can be a disadvantage, since dirt collects in the twists and must be removed by vigorous washing.

The quality of cotton depends on the staple length, the number of convolutions, and the brightness of the fiber. Long-staple cotton has about 300 convolutions per inch, while short-staple has less than 200. Cotton fibers vary from 16 to 20 microns in diameter. 9

When cotton is Mercerized by treatment with caustic soda (sodium hydroxide, an alkali), the fibers are somewhat straightened and swollen; the lumen then becomes more readily visible under the microscope. The electron microscope is a research tool used to disclose structures invisible under the optical microscope. The cellulose walls of the cotton fiber are disclosed as a series of concentric growth rings somewhat similar in appearance to the growth rings in a tree stump. Within the rings minute fibrous deposits called fibrils have been laid down in a lattice formation. It is due to the physical variations of the lengths of the individual fibrils, particularly those near the surface or cortex of the cotton fiber, that some of the important chemical and physical properties of cotton occur. 10

Chemical Composition: Molecular Structure

It is customary to classify the natural textile fibers into sources of origin such as animal, mineral and vegetable but conservators will find that a better way is to assign them into chemical divisions because it helps them to predict weaknesses and safe handling methods. This permits a scientific systemization of the necessary knowledge.

Cellulose is an example of a single chemical compound that will yield a large variety of fibers. Natural cellulose fibers, such as cotton, flax, jute, hemp, and ramie are built up by nature during the growth of the plant and come from the seed, the stem, or the leaves.

Of all the fibers we may encounter, cotton and well made paper are probably the most nearly pure cellulose. Cotton differs because it is a

10Labarthe, Textiles: Origins to Usage, p. 141-42.
Figure 1. Idealized microscopic appearance of cotton fiber.

seed hair type of unique cellular structure. Other vegetable fiber substances made from the stalks and leaves of plants such as flax (linen), hemp, ramie, jute, wood, bark, and many others are called bast fibers. Although both cellulosic fiber types contain some impurities such as waxes and minerals, the bast fibers are more apt to contain lignins and ligno-cellulose which are physically weaker and react differently with certain other substances than pure cellulose. A case in point is that ligno-cellulose is faintly acidic and for that reason tends to accept basic dyes, whereas true cellulose does not. Because the cellulose forms the bone structure of the plant in the bast fibers, the cellular form is apt to be long with channeled pores. This feature helps to explain differences in physical behavior between the bast and the seed hair type. 11

The basic unit of the cellulose molecule is the glucose unit. The glucose unit is made up of the chemical elements carbon, hydrogen, and oxygen.

Figure 2. The Cellulose Molecule

Figure 2 shows how these elements are arranged in the Glucose unit. It also shows two glucose units joined together to form the cellobiose unit characteristic of cellulose.

The cellulose molecule is a long linear chain of glucose units. (See Figure 3)

Figure 3. A Molecule Chain
The number of units in the chain depends on the origin of the cellulose. Natural and regenerated cellulose differ in the length of the molecule chain. Fibers with long molecular chains are stronger than those with short molecular chains. Polymerization is the process of joining small units together. The large unit is then called a polymer.

The chemical reactivity of cellulose is related to the three hydroxyl groups (OH groups) of the glucose unit. These groups react readily with moisture, dyes, and special finishes. Chemicals such as bleaches that cause a breakdown of the molecule chain of the cellulose usually attack the oxygen atom and cause a rupture there. 12

Constituents of Cotton
Raw cotton contains, in addition to cellulose, the usual constituents of a vegetable cell. These are oil and wax, pectoses and pectins, proteins and simpler related nitrogen compounds, organic acids, mineral matter, and natural coloring matter. The approximate composition of raw cotton is as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>85.5%</td>
</tr>
<tr>
<td>Oil and Wax</td>
<td>0.5%</td>
</tr>
<tr>
<td>Proteins, Pectoses, and</td>
<td></td>
</tr>
<tr>
<td>Coloring matter</td>
<td>5.0%</td>
</tr>
<tr>
<td>Mineral matter</td>
<td>1.0%</td>
</tr>
<tr>
<td>Moisture</td>
<td>8.0%</td>
</tr>
</tbody>
</table>

13 Trotman, *Dyeing and Chemical Technology of Textile Fibres*, Third, ed., p. 38
Fiber Properties

Abrasion resistance
The cotton fibers can be spun into firm, tightly twisted yarns or soft, fluffy ones. The fabrics woven from cotton will determine the resistance to abrasion. Cotton fabrics are generally recognized as being long-wearing, due to good abrasion resistance.

Absorbency (Hygroscopic Moisture)
Raw cotton contains from five to eight percent of hygroscopic moisture; most scientists place the figure at seven to ten percent under standard conditions. This moisture is held in the pores and in the surface of the fibers and depends largely on the atmospheric humidity.

Chemical Reactivity
Mildew readily attacks cotton.

Mineral Acids (Sulphuric, Hydrochloric, Nitric, Hydrofluoric)
Concentrated acids will destroy. Cold dilute acids do not injure if washed out or neutralized. Dilute solutions (3 percent or less) of these acids, if allowed to dry, will make fiber tender and will ultimately destroy it.

Volatile Organic Acids (Formic, Acetic)
Will cause no detrimental action.

Non-Volatile Organic Acids (Oxalic, Tartaric, Citric)
Will tender slightly if not removed, especially if heat is applied.

Strong Alkalies (Caustic Soda, Soda Ash)
Will cause no injury, even if concentrated or if heat is applied when air is excluded. Concentrated solution will mercerize if cotton is under tension; otherwise cotton will shrink.

Weak Alkalies (Ammonia, Boraxo, Phosphate of Soda, Silicate of Soda, Soap)
Cause no injury.

Oxidizing Agents (Potassium Permanganate)
Will destroy if not controlled.

Metallic Salts
Cotton has practically no affinity for metallic salts.

Bleaching Agents (Chlorine or Hypochlorites)
Cold dilute solutions are not detrimental to fiber. It must be removed or washed out completely as heat and concentrations will destroy fiber.

Other Oxidation Bleaches (Hydrogen Peroxide, Sodium Perborate, Bisulphite of Soda)
Causes no injury if controlled.
Reduction Bleaches (Sulphurous Acid, Hydrosulphite)
Causes no injury if controlled.

Crimp
Natural or inherent crimp occurs in cotton. Cotton has a two-dimensional twist called convolutions.

Cohesiveness
The twist formed within the cotton fiber makes a natural crimp that enables the fibers to cohere to one another, so that despite its short length, cotton is one of our most spinnable fibers.

Density (Specific Gravity)
1.48 grams per C.C.

Elasticity
The elasticity of cotton is largely due to the physical form of the fiber. The maturing of the cotton causes the fibers to flatten and twist. This twisted and bent structure of the fibers gives them a small amount of elasticity. It is lower than silk or wool; but better than linen.

Dyeability
Is less than that of silk and wool. However, cotton will readily take the most color-fast of all dyestuffs and in greater variety of colors. Color fastness to sunlight, washing, crocking and other conditions depends, of course, more upon the nature and permanence of the dyestuff than upon the identity of the fiber.

Classes of Dyestuffs Met with in Common Use
Direct, Sulfur, Basic with mordant, Coloring matter developed on fiber, Vat colors.

Electrical Conductivity
Is a good conductor of electricity; does not build up static.

Elongation
6-7 percent elongation at break

Flammability
Cellulose fibers ignite quickly, burn freely, have an after-glow, and gray feathery ash.

Heat Conductivity
Cotton is ranked as cooler than wool or silk, but not as cool as linen. The fabric structure plays a more important part in the warmth or coolness of fabrics than does the conductivity of the constituent fibers.
Heat Sensitivity
Cotton is quite resistant to damage by heat. It can be pressed with a hot iron without scorching. At 475° F., it turns brown and burns.

Luster
The untreated fiber has no pronounced luster. This quality is readily imparted to cottons by means of the mercerization finishing process. Mercerized cotton fabrics are almost as glossy as silk.

Loft
Resiliency of the fiber and fabric, and warmth go together to the extent that the more resilient fiber will retain its loft for a longer period of time during laundering. Cotton is not as resilient as wool; it has a low resiliency. Cotton weaves easily into compact structures, however fabrics will wrinkle badly.

Stability
Cotton has a natural shrinkage of approximately five percent. It can be given a special finish, sanforizing, by which the shrinkage can be controlled within one percent.

Stiffness
Cotton is about at the intermediate point between the most stiff fibers, such as glass, hemp and jute, but being firmer and more self-supporting than nylon, rayon and wool. Cotton is also classed as a tough fiber and is one of the best in durability.

Strength
A single cotton fiber has a low tensile strength. It will support a dead weight of from 2 to 8 grams. The finished cloth can be made strong and durable by using tightly twisted yarns compactly woven together. Mercerized fabrics are made stronger. Cotton is stronger when wet than when dry.

Sunlight Resistance
Like all cellulose fibers, cotton is weakened by the ultra-violet rays of sunlight. The tendering action is due to the formation of oxycellulose.  

Silk

History
Chinese legends tell us that silk was discovered in 2640 B.C. by a Chinese empress. The Chinese carefully guarded their secret of the silk

cocoon for 3,000 years. They wove beautiful fabrics and sold them to
Eastern traders, who carried them back to their own countries where they
were prized very highly. Thus, a very great demand for silk was created.
In A.D. 300 refugees from China took cocoons to Korea and started raising
silkworms. Japan learned about silk production from the Koreans. The
industry spread through central Asia into Europe, and by the twelfth
century, Italy was the silk center of Europe. This leadership was taken
over by France in the seventeenth century. Weaving of silk became important
in England when many Huguenot weavers emigrated from France to England in
1685.

Sporadic attempts to cultivate silk have been made in the United
States. The charters of the various colonies stipulated that a silk
industry must be started. Because of climatic conditions, the North was
not able to grow mulberry trees; and in the South, growing cotton, which
was also needed by the mother country, was much more profitable. But as
late as 1933, some manufacturers of silk tried raising silkworms.

During World War II, the government froze the import and production
of silk in this country. The existing fibers were reserved for use by
the armed forces. Our supplies from Japan and China were cut off, and
during the decade from 1939 to 1949, we were without silk.

The introduction of nylon for hosiery took away much of Japan's
market for silk. Another threat facing the silk industry today is a labor
shortage due to technological progress. The industry has relied in the
past on women from farm families for its labor force. With agricultural
prosperity and industrialization in Japan, it is no longer necessary for
women to do this work to maintain minimum survival for their families.
Silk production has largely been a household operation, and for production
to survive, it will be necessary to combine and systemize these small
operations - to develop organizations similar to the cooperatives in the
United States. Unless these changes are made in the industry, it is
predicted that silk will be so expensive that it will become a luxury
fiber like vicuna.

Silk can be produced in any temperate climate, but it has only been
successfully produced where there is a cheap source of labor. Silk is a
continuous filament, protein fiber produced by the silkworm. Cultivated
silk is obtained by a carefully controlled process in which the silkworm
lives a coddled and artificial life especially for the purpose of producing
fibers. *Wild silk* production is not controlled; instead, these silkworms feed on oak leaves and spin cocoons under natural conditions.

**Production of Silk**

Sericulture, the production of the worms, their development, and the spinning of the cocoon, is largely a home industry. In the modern scientific industry the tiny eggs or seeds are deposited by the carefully bred female moth on cards or strips of cloth. The eggs are incubated by mild warmth: they are covered with a blanket or worn inside the workers clothing until the tiny ants or silkworms are hatched. These ants are a day-and-night care. The young ants are provided with shredded, fresh, tender mulberry leaves (*Morus alba*). The leaves to which the worms cling are lifted to the feeding trays. The weak worms are discarded. The worms are kept in a room at a uniform temperature, they are fed five or six times a day, and the trays are kept clean.

The ants are initially about three millimeters long. During its growth, the worm sheds its skin four times, at about 5-day intervals. After the fourth shedding, it develops for about ten more days. The fully grown worm is 8 to 9 centimeters in length and has increased its weight by a thousand-fold to five grams.

The fully developed worm has a total life period of approximately a month. It first learns to eat and begins to seek something on which to spin its cocoon. This worm is then transferred to a wooden frame containing twigs or straw, on which the cocoon is spun. To spin this cocoon the worm spins a net and then forms a shell around his body. The worm swings its head in a figure-eight formation and expels fluid from two sacs in its body. The two strands are excreted from minute openings, or spinnerets, close together in the lower jaw. The fluid solidifies when in contact with the air. The two filaments, known as fibroin, are cemented together by a glue known as sericin. The sericin is excreted from two glands. The worm makes more than one movement with its head each second and can be heard at work even after the cocoon has become so thick that the worm cannot be seen. It takes two or three days to complete a cocoon. The worm then changes into a pupa or chrysalis.

In about two weeks the moth will develop if the chrysalis is permitted to live. The moth escapes through the bottom of the cocoon and breaks the 

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silk strands in the several layers to make its escape. An alkaline solution secreted by the moth allows it to break the strands more easily. It is customary to permit the development of only enough moths for breeding and egg-laying, because the broken cocoons are of less value than those having long, unbroken filaments. In order to produce unpierced cocoons the chrysalis is killed by heat in dry air, more rarely by hot water or steam. The cocoons are weighed; the female moths, being heavier, can thus be selected and allowed to escape. The moths live only a few days, during which they mate, and the eggs, about 700 from each female, are laid on the cards or sheets. Thus the cycle begins once more.

Wild silk is that produced from other types of moths, which have not lent themselves to domestication. These cocoons must be sought in the trees, and many of them have already been pierced when found. Wild silk is less uniform, but is coarser and somewhat stronger than the cultivated variety. The most common wild silk is that from the tussah or tussar silkworm of Asia. This worm feeds on mulberry, oak, and other trees. The term is generally applied to all wild silks, but strictly speaking, the tussah is an Indian silkworm.

The Making of Raw Silk

The unpierced cocoons are sorted according to color and texture before the reeling or unwinding operation. The reeling is still done much the same as the Chinese peasants have done for centuries. Even in the modern filature, the reeling depends upon the sight, touch, and skill of the reeling person.

Several cocoons are soaked in a basin of water at about 140° F. in order to soften the gum or sericin. The outer filaments are coarse and tangled and make up waste silk. The filaments of four or more cocoons are drawn together to form a single strand of uniform diameter. Six ends are commonly used to make the 1-1 denier size yarn widely used in the United States. The ends are drawn through a small glass or porcelain orifice to form a thread as nearly smooth and uniform as possible. Because the filament of each cocoon is not uniform, the reeler must cast on or take off ends to produce a strand with as few thin spots, knots, or loose filaments as possible. The cocoons, being unwound, bob up and down in the basin as the figure-eight cast filaments are pulled and are held down only by the water adsorbed. Each cocoon contains between 300 and 1,000 yards of fiber which can be reeled. The inner portion is too weak to be reeled and
this portion and the outer portion brushed off by the beaters are known as frisons and constitute waste silk. The reeled thread is wound onto a reel operated by hand or foot power in homes or filatures, and by steam power in large filatures or factories having several hundred basins. The price of the raw silk threads depends to a considerable degree upon the quality of the cocoon and the manual skill of the reel person. No device has yet been perfected which will consistently produce a quality as fine as the reeler can make, or as economically.

The reeled silk, twisted to form a strong thread, the waste silk from the discarded portions of the cocoons (about half the filament length), and the fibers from the pierced cocoons, make up the silk of commerce. Skeins of reeled silk weighing 50 to 100 grams each are wrapped in bundles called books, which weigh from 5 to 10 pounds each. These books of Japan and China silk are packed in picul bales weighing one picul (133 1/3 pounds). Italian silk bales weigh about 200 pounds. The bales of silk from the Orient are covered with tea matting and shipped all over the world. Before World War II, the United States imported approximately 85 percent of Japan's raw silk. The classification of raw silk grades is a loose one, and there is no generally accepted standard. Silks are graded for uniformity by visual examination by commercial laboratory technicians.

Silk Yarn

The raw silk strands are transformed into a yarn by throwing. This consists of increasing the twist or adding more strands and twisting them together. This thrown silk is wound on spools or twisted into skeins and is then ready for weavers. Singles are strands consisting of from 3 to 8 or more double filaments twisted together to form a yarn suitable for either warp or filling yarns or for knitting. Tram silk consists of two or more strands of singles slightly twisted together. Organzine is formed by twisting two or more singles strands in the opposite direction to the twist of the singles. This is the usual warp yarn and is commonly made from the best fibers.

The skeins are usually soaked in a soap solution before throwing in order to remove the sericin gum still contained in the raw silk to an amount of approximately 25 percent. The different grades are tinted in different shades during soaking so that they can be more readily identified in future handling.

The count and size of reeled thrown silk is based on the denier
A denier is a legal coin of weighing 0.05 grams. The size is expressed as the weight in deniers. Thus denier is the weight in grams of 9000 meters of yarn or filament. The weight is subject to a correction of 25 percent to allow for the sericin removed in the degumming bath.

Spun Silk Yarn

The waste silk is made into spun silk yarn by the same process as the yarns from other short fibers are fashioned. The pierced cocoons, wild cocoons, and the frisons or waste compose the raw materials for spun silk. The silk is degummed by boiling off in soap suds. It is then dried and cut into 9-inch lengths. The cut fibers are combed in order to straighten them, and they are then rolled several times in the drawing frame. The yarns are twisted on a spinning frame, which gives them a tighter twist than is needed for the long-filament thrown silk yarn. The spun silk yarn is less lustrous than thrown silk because of the tighter twist, and it is less elastic and strong and has a harsher feel or handle.

Silk Weighting

Silk is purchased in the raw state on a weight basis, and the 20 to 30 percent of gum it contains is charged for as if the yarn were all silk. It is customary to replace with metallic salts some of this gum which has been boiled off before the yarn can be dyed. Silk has a great affinity for the salts of tin and iron and for tannin. An insoluble tin phospho-silicate is the usual weighting material. A pure silk or pure dye silk is one which is containing no more than 10 percent of weighting, except in black silk, which can have 15 percent.

Heavily weighted silks containing in excess of 40 percent are not serviceable. The tensile strength is low, the fibers are inelastic, sunlight rapidly deteriorates the fibers, and the fabric is difficult to wash and dry clean. 16

Types of Silk

Silk refers to cultivated silk.

Wild or tussah silk is a tan-colored fiber from the uncultivated silkworm, which feeds on scrub oak. As the cocoons are always pierced, the fibers are shorter than reeled silk. Shantung, pongee, and honan are fabrics made from wild silk.

Duppioni silk comes from two silkworms who spin their cocoons together. The yarn is uneven, irregular, and larger is diameter.

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16 Labarthe, Textiles: Origins to Usage, pp. 208-17.
Raw silk refers to cultivated silk-in-the-gum. Raw silk varies in color from gray-white to canary yellow, but since the color is in the sericin, boiled-off silk is white. The term is often incorrectly used to describe spun silk. Reeled silk is the long continuous filament, 300 to 1,800 yards in length. Spun silk refers to yarns made from staple fiber from pierced cocoons and waste silk. Waste silk is composed of the tangled mass of silk on the outside of the cocoon and the fiber from pierced cocoons.  

Structure

Silk is the only natural filament. It is a solid fiber; but unlike the man-made fibers it is not uniform in size. The filaments are 300 to 1,800 yards long. In cross section, the fibers are like triangles with rounded corners. The rod-like, almost circular fibers are responsible for the luster and smoothness of silk. The diameter of silk fibers ranges from 2 to 5 microns, making it the finest of the natural fibers. The approximate average denier per filament is 1.2.

The silk fiber is a double strand held together by a gum or sericin, a water-soluble substance secreted by the silkworm. This sericin is a very important part of the silk fiber. It serves as a warp sizing for the silk yarns as they are threaded on the loom and woven into the "gray goods" cloth. Because of the sericin, the silk yarns can be used without twist (zero twist). When the sericin is removed from the fiber in the degumming process (about 25 percent weight loss,) the fabric structure becomes more mobile. The low twist and the mobile structure are major factors in the "dry" tactile hand and the liveliness, suppleness, and drape of silk fabrics. Zero twist yarns are important in the good covering power exhibited by silk.  

Fiber Properties

Abrasion Resistance

High-medium strength, tough.

Absorbency (Hygroscopic Moisture)

The silk fiber is capable of adsorbing from 10-30 percent of moisture. Like wool, it still feels comparatively dry in spite of the moisture it

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18 Ibid.
Figure 4. Idealized microscopic appearance of wild silk fiber.

Figure 5. Idealized microscopic appearance of cultivated silk fiber.

has adsorbed. The regain of silk is 11 percent.

**Chemical Reactivity:**

**Mildew**
Silk is rarely attacked by mildew.

**Mineral Acids** (Sulfuric, Hydrochloric, Nitric)
Concentrated mineral acids will dissolve silk completely. The application of heat causes the silk to dissolve more rapidly. Cold dilute acids, except hydrochloric, will not injure silks.

**Volatile Organic Acids** (Formic, Acetic)
Formic and acetic acids have no injurious effect on silk unless heated.

**Strong Alkalies** (Caustic Soda, Caustic Potash)
Have slight action on silk in cold concentrated solutions. Heated solutions completely dissolve silk.

**Weak Alkalies** (Ammonia, Boraxo, Sodium Phosphate, all common detergents)
Attack silk more readily than they do cotton and linen. Free alkali must be avoided in washing.

**Metallic Salts**
Metallic salts replace the boiled off sericin before the yarn can be dyed.

Silk has a great affinity for the salts of tin, iron, and tannin.

**Bleaching Agents** (Chlorine and Hypochlorites)
These yellow and tender silk.

**Other Oxidation Bleaches** (Hydrogen peroxide, Potassium permanganate)
May be used on silk if a suitable reducing agent is used as an after-treatment and a thorough rinsing follows.

**Reduction Bleaches**
May be used, followed by thorough rinsing.

**Cover**
Zero twist yarns are important in the good covering power exhibited by silk.

**Cohesiveness**
Not applicable as silk is a filament.

**Density** (Specific Gravity)
1.30 grams per C.C.

**Dyeability**
Silk has a greater affinity for dye than has any other textile fiber. It adsorbs dyes at a low temperature, and, being a protein, it possesses both an acid and a basic property and can therefore be dyed with basic or acid
dyes.

**Elasticity**
Silk is very elastic, and the fiber can be stretched from 1/17 to 1/5 of its length before breaking.

**Electrical Conductivity**
Silk is a poor conductor of electricity. It is electrified by friction in the manufacturing operations, and the difficulty is lessened by maintaining standard conditions of 65 percent relative humidity and 70° F.

**Elongation**
Silk has 20 percent elongation at break.

**Flammability**
Silk fuses and curls away from flame. It burns slow, and is sometimes self-extinguishing. Has a crushable black ash and the odor of burning hair.

**Hand**
The low twist and mobile structure are major factors in the "dry" tactile hand and the liveliness, suppleness, and drape of the fabric.

**Heat Conductivity**
Even very fine silk is a poor conductor of heat. Garments made from silk are warmer than those of rayon, cotton, or linen. Weighted silks containing metallic salts permit the conductivity of heat and are therefore less warm.

**Heat Sensitivity**
If white silk is heated in an oven at 231°F. for 15 minutes, it begins to turn yellow. The use of too hot an iron in pressing will similarly yellow silk. Above 330°F. silk disintegrates.

**Luster**
The lusterless raw silk is given a soft, rich luster after the gum is removed. The rod-like, almost circular fibers are responsible for the luster and smoothness of silk.

**Loft**
The resiliency of the silk fiber enables silk fabrics to keep their shape and makes them resistant to wrinkling.

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Chemical Composition

Raw silk consists of fibroin and sericin or glue. The cultivated silk also contains small quantities of fats and waxes, which are removed with the sericin in the degumming boil-off. Raw silk is described as containing the following constituents:

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fats and Waxes</td>
<td>3.02%</td>
</tr>
<tr>
<td>Sericin</td>
<td>22.28%</td>
</tr>
<tr>
<td>Fibroin</td>
<td>73.59%</td>
</tr>
<tr>
<td>Ash or mineral matter</td>
<td>1.11%</td>
</tr>
</tbody>
</table>

The fibroin or actual silk fiber is a protein substance made up of the following elements:

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>48.3%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.5%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>19.2%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>26.0%</td>
</tr>
</tbody>
</table>

Colorants

Until 1856, natural dyes and pigments were used as coloring agents. These dyes and pigments were obtained from plants and insects. When Perkin, a young chemist, discovered mauve, the first synthetic dye, a whole new industry came into being. All over Europe chemists started to develop synthetic dyes and it was not until World War I, when our trade with Germany was cut off, that a dye industry was developed in the United States.

Pigments are insoluble color particles that are held on the surface of a fabric by a binding agent. Their application is quick, simple, and economical. Any color can be used on any fiber, since the pigments are held on mechanically. Stiffening of the fabrics, crocking, and fading are some of the problems encountered.

Dyes must be in small particles that can be thoroughly dissolved in water or some carrier in order to penetrate the fiber. Undissolved particles stay on the outside and the colors then have poor fastness to crocking and bleeding.

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20 Labarthe, Textiles: Origins to Usage, p. 219
Pigments

A pigment is a finely divided, colored substance which imparts its color effect to another material, either when mixed intimately with it, or when applied over its surface in a thin layer. When a pigment is mixed or ground in a liquid vehicle to form a paint, it does not dissolve, but remains dispersed or suspended in the liquid. Colored substances which dissolve in liquids and impart their color effects to materials by staining or being adsorbed are classified as dyes.

The various methods of painting - oils, water color, etc. - differ from one another in the material with which the color is applied and attached to the ground; the pigments used are the same in all, except that a pigment which is suitable for one purpose does not always meet the requirements for another.

Classification of Pigments

Pigments may be classified according to color, use, permanence, etc. It is customary, however, to classify them according to origin, as follows:

A. Inorganic (mineral)
   1. Native earths: ochre, raw umber, etc.
   2. Calcined native earths: burnt umber, burnt sienna, etc.
   3. Artificially prepared mineral colors: cadmium yellow, zinc oxide, etc.

B. Organic
   1. Vegetable: gamboge, indigo, madder, etc.
   2. Animal: cochineal, Indian yellow, etc.
   3. Synthetic organic pigments

General Characteristics of These Groups

Artificial mineral colors made with the aid of strong heat are generally of the greatest permanence for all uses, while those requiring delicate or very accurately balanced processing are less so. The artificial counterparts of the red and yellow earths are more brilliant and, if well prepared, superior in all other respects to the native products. In general, pigments derived from natural sources are less permanent than the average synthetic color. The synthetic organic pigments are characterized by a great brilliance and intensity. Some of them are remarkably permanent, but many others, particularly the older ones, are fugitive and have the defect of bleeding in oils. Many require the
addition of inert bases during manufacture.

The native earths used as pigments occur all over the world, but there is always some special locality where each is found in superlative form or where conditions have been established which permit of its being purified to a greater or more uniform extent than is economically possible elsewhere. Substitutes for French ochre, Italian sienna, etc., are offered for reasons other than the purpose of supplying the best available product.

The natural impurities in some red earths are many times harmful; therefore the artificial red oxides are preferred to them. The impurities or non-coloring constituents of the highest grades of ochre and the other permanent earth colors seldom present the same disadvantages.

The artificially prepared colors of American makes, are equal if not superior to any other. Cobalt yellow, cerulean blue, cobalt green, and Naples yellow are made in very limited amounts almost entirely for artists' use and are therefore not produced in this country for economic reasons. European books still describe defects in pigments which have long since been overcome by American manufacturers.

There is some doubt as to the antiquity of the practice of refining, calcining, or otherwise treating the native earth pigments. Under the name of artificial or manufactured cinnabar, Theophrastus described the purification and improvement of a fine variety of native red iron oxide and noted that it was a recent innovation, only 90 years old (fourth century, B.C.). All the more complete records from Roman times on, show that the procedures of calcination and levigation of the native earths was common practice. The identification of pigments found in ancient relics is not particularly difficult for the experienced technician and many studies have been made of them.

Lakes. A lake is a pigment which has been made by precipitating or fixing a dye upon an inert pigment or lake base. The process may be compared to that of dyeing cloth and a high degree of skill is required to produce good results. Lakes are made in a great range of hues and strengths. A toner is an organic pigment in its most concentrated form, containing no

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22 Powdered materials which become colorless or virtually colorless in paints are called "inert-pigments" - a technical term or classification which has no reference to chemical inertness or stability.
inert pigment; for satisfactory performance in artists' colors it often requires added inert pigment to contribute bulk to the paint and to decrease excessive tinctorial power. Alumina hydrate is the usual base for clear, transparent lakes such as are used as glazing colors, in printing inks, etc.; while blanc fixe is the best base for those to be used in heavy paints and for similar purposes where more body or opacity is required. Cheaper lakes, less clear in tone, are made on clay, barytes, etc., Green earth is valuable as a base for green lakes, as it is a species of clay which has a strong power of adsorption for dyes. A lake is also occasionally made with a colored pigment as a base; for example, Tuscan red, a pigment made for industrial use, is made with alizarin on an Indian red base.

The dyestuffs used are synthetic products, although a few of the older extracts of vegetable and animal origin still survive for some special purposes (usually only because of their low cost).

Lakes made from modern organic colors are greatly superior in every paint requirement to those obtained from the natural coloring extracts. Prior to the eighteenth century, lake usually meant red lake only. The term comes from the Indian lac which is described under shellac.\(^{23}\) Scum or sediment from the dyers' vats, called lacca and consisting of dyed particles of shreds, fibers, dust, and other impurities, was collected and used as a pigment in Italy in early times.

**Reduced or Let-down Colors.** Commercial pigments are supplied for some industrial purposes in grades known as reduced or let-down colors. As a general rule they are condemned for use in artists' paints, none but the purest, most concentrated grades available should be selected for use in permanent painting.

A reduced pigment is not ordinarily diluted with inert filler by the simple admixture of dry powders, but the inert material is usually introduced during the striking of a batch in the wet stage, thereby producing such an intimate mixture that the product has a brighter and less muddy tone than it would have had if the filler had been merely

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\(^{23}\)Shellac is obtained from the branches and twigs of several species of trees in India, where it is deposited by insects which feed on the sap of the trees. The crude material or stick-lac is refined into a number of grades for various purposes. The less refined grades (seed-lac, garnet-lac, and button-lac) are a deep blood-red; formerly this lac was used to make a red dye, and before synthetic dyes superseded it this was the principle object of its cultivation, shellac for varnish being a by-product.
sifted into a ground together with the finished dry color. A reduced color is often marketed under the name of the color followed by the percentage of its pure pigment content, and pure pigment color of a type that is also largely used in let-down form (such as Prussian blue) is often labeled "C.P." (not meaning chemically pure in this case, but merely denoting full strength), an improvement over the former use of superfluous names for various grades.

**Mass Tone** and **Undertone.** The full-strength surface color of a pigment viewed by reflected light is called its mass or top tone; its color effect when it is spread out thinly is called undertone. The undertone is discerned when a transparent color is spread out on glass and viewed by transmitted light or when an opaque color is used as a tinting color, diluted with much white. Some pigments have undertones which are distinctly different from their top tones; this is apparent in the average alizarin when it is viewed in a thin layer on glass held up to the light, or drawn out on paper. Some synthetic organic reds used as industrial printing ink colors have such bluish undertones that they can be used to produce two-toned effects. Other pigments display little or no differences between their top tones and their undertones. The paint chemists generally use the term "mass color" instead of "mass tone".

**Composition of Pigments.** It should be noted that the chemical purity of pigments varies greatly; some are simple, almost pure compounds as described; others of equally high quality contain minor components either as natural impurities or as the result of ingredients, added during manufacturing, to modify color or pigment properties.

**Nomenclature.** Pigments are named for their resemblances to objects in nature, for their inventors, their places of origin, the purposes for which they are used, and for their chemical compositions or derivations.

For centuries the nomenclature of pigments was confusing and unsystematic. The principal cause of confusion was the labeling of colors with arbitrary names by manufacturers and others, often for some ulterior motive. This has caused a single color to be known by a dozen different names and two or more entirely different colors to be known by the same name. Proposed systems of rational color nomenclature never made any great headway until the 1940's when the situation was clarified in the United
States by the adoption of the Paint Standard. 24

As a general rule, the manufacturer of a prepared or mixed color or similar material sold under a trademarked name or under some indefinite designation such as "permanent green" or "primrose yellow", is not at all bashful about revealing its true composition (when it is made of high-grade, approved ingredients), because he thereby gets credit for the use of correct or expensive raw materials. Products whose composition is kept secret have the disadvantage of being under suspicion. The artist who is concerned with the permanence of his work is advised to select only those colors whose pigment origin is clearly indicated by name, and, for the maintenance of our rational nomenclature, to reject colors whose nomenclature does not conform to that of the Paint Standard. 25

Polymer Colors

Artists' Colors Based on Synthetic Resins. The following materials are the principal artists' mediums that have been developed in the mid-twentieth century. Their criteria of excellence are taken directly from the performance of similar products in the industrial coating-material field. So far, our knowledge of their ultimate values in fine-arts painting is somewhat limited. We have no long-term experience to guide us in the best ways to apply polymer colors or in the many details of composition and manipulation that ordinarily accumulate over the years of experience. After a decade of use, however, these colorants have lived up to their technical expectations, and no serious technical faults have developed.

Polymer Colors. The most widely used artists' colors based on synthetic resins are the so-called polymer colors, made by dispersing pigment in an acrylic emulsion. These colors are thinned with water, but when they dry, the resin particles coalesce to form a tough, flexible film that is impervious to water.

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24 The Standard was published by the National Bureau of Standards as the result of work completed in 1938 by the Paint Testing and Research Laboratory of the Massachusetts Art Project, WPA, under the direction of Frank W. Sterner and Rutherford J. Gettens. It is not a government regulation, but was arrived at by conference and voluntary agreement by leading American manufacturers, artists, and other interested persons. A standing committee on which manufacturers and artists' organizations are represented meets periodically for revisions.

The polymer colors have a number of excellent qualities for which they have become popular. When they dry, they lose their solubility very rapidly. They may be made uniformly mat, semi-mat, or glossy by mixing them with the appropriate mediums. They are non-toxic, and because their thinning solvent is water, they may be used by persons who are sensitive or allergic to the volatile solvents.

The name, polymer colors, has been adopted by general agreement. Although it is not specifically descriptive (since virtually every film-former is a polymer of some sort), it serves well to distinguish them from other paints made from synthetic resins, and it also replaces such loose terms as the "acrylics" or "plastic paints". Polymer colors are extremely versatile in imitating or approximating all the effects of the traditional water media. They are the first paints since oil colors that are sufficiently flexible to be used on canvas. With no other medium can a full-bodied, freely-stroked or "juicy" effect be obtained with such dispatch. But polymer colors are not a complete substitute for oil paints, and artists whose styles require the special manipulative properties of oil colors: finesse and delicacy in handling, smoothly blended or gradated tones, or control in the play of opacities and transparencies, find that these possibilities are the exclusive properties of oil colors. The polymer colors, however, are a boon to those painters seeking a high rate of production. A painting that might have taken days to accomplish in oil (because of the necessity of waiting for layers of paint to dry), can be completed in one session. The pigments are identical to those used in oil, except that the only white used is titanium. An occasional pigment that works well in oil and water color is not compatible with the usually alkaline nature of the polymer medium, and so will not be found in the polymer palette. The medium confers on the pigments a definitely more brilliant or vivid quality than they exhibit in oil paint. They are sold both in tubes and in jars. The colors in the jars are usually a bit more fluid than the tubed kind. Polymer paint films have extraordinary flexibility, an almost rubbery elasticity, which they retain without appreciable embrittlement for a long period of time. An oil-paint film would lose a measurable degree of its flexibility during the same period of aging.

Although all the brands of acrylic polymer colors are made from the same emulsion-polymerized acrylic resin (Rhoplex A34), their manufacturers
use a variety of additives to enhance their working properties and stability. For this reason not all the colors of different manufactured colors can be intermixed freely without curdling of the vehicle. However, a simple test will determine which colors will mix with one another: thin each of the two colors with about an equal volume of water and mingle them with a clean brush on a strip of glass. Close examination while the colors are still wet, by both direct and transmitted light, will disclose any tendency to curdle.

List of Pigments I Use (All in the form of Liquitex® Acrylic Colors)

Yellow Ochre: A clay colored by iron and produced in a number of dull yellow shades. It is opaque and absolutely permanent. The best, most carefully washed and refined grades come from France. Its use dates from prehistoric times.

Cadmium Orange: Cadmium seleno sulfide coprecipitated with barium sulfate, made in a variety of shades, all bright, very opaque, and permanent. It is traditional orange of the artist's palette.

Cadmium Reds: Cadmium Seleno-sulfide coprecipitated with barium sulfate.

Cadmium Red Light: A brilliant light red toward the yellow-red range. It is a key palette color, very opaque and permanent.

Cadmium Red Medium: A deeper and bluer red. It has good brilliance as a concentrated color but, like all the deeper cadmium reds, makes mixtures with white that are much muddier than tints of the organic reds. Very opaque and permanent.

Cerulean Blue: Cobaltous stannate, a compound of cobalt and tin oxides. It is a middle blue of medium color depth with moderate brilliance. Glass-like ceramic pigment with some degree of luminosity, highly stable and lightfast and quite opaque. Known as early as 1805. Introduced by George Rowney, England, in 1870 under the name Coeruleum, derived from caerulem, Latin for sky-blue pigment, applied by the Romans mainly to Egyptian blue.

Cobalt Blue: Compound of cobalt oxide, aluminum oxide, and phosphoric acid. It is a middle blue, deeper than cerulean, that is completely stable and lightfast. Cobalt blue is a ceramic pigment of which the crystalline structure yields a certain degree of luminosity despite only moderate brilliance and is nearly transparent. Discovered by Thenard, France, 1802; introduced as an artists' color 1820-30.

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**Ultramarine Blue:** Genuine ultramarine pigment. Originally this color was made by grinding a semi-precious stone, lapis lazuli, and purifying it by a complex and difficult process, thus removing all the gray rock with which it is usually associated. Genuine or lapis ultramarine is a rich, deep "true blue" of practically uniform hue. It has been found in Assyrian and Babylonian relics but only as a decorative or precious stone. Its European use as a pigment began in the twelfth century; it has always been one of the costliest and most precious of painting materials. Lapis Lazuli occurs in Persia, Afghanistan, China, Chile, and a few other countries; it is more often found in the form of blue particles and veins scattered through a gray rock than in the solid pieces which are used in jewelry and ornaments. Investigators believe that lapis is the sapphire of the Bible and other early writings, including those of Theophrastus and Pliny.

Since 1828, the ultramarine of commerce has been an artificial product made by heating clay, soda, sulphur, and coal in furnaces; the color of the resulting compound is attributed to colloidal sulphur. Best grade American ultramarines are produced in a wide variety of shades, from that of the true ultramarine blue to imitation cobalt and turquoise shades which are comparatively greenish. The pigment called green ultramarine is a rather dull color with properties the same as those of ultramarine blue; it is produced during the manufacture of the blue, and may be considered unfinished ultramarine blue; it is not widely used. All pure ultramarine pigments and variations are equally permanent, but many inferior and reduced grades are made for industrial uses. Ultramarine is semi-transparent; it works poorly in oil, where it tends to yield stingy instead of buttery pastes. It is entirely permanent for most uses, including high temperature processes, but is easily affected and bleached by very weak acids and acid vapors. The same is true of the native lapis. After several independent discoveries concerning the nature of the product and the method of its manufacture, it was first produced commercially in France by Guimet in 1828. The pigment was used by artists in Paris. In the same year the process was published by Gmelin in Germany.

**Hooker's Green:** Ferric nitroso betanaphthol. This "Hooker's Green" made with a newer pigment is an intense, beautiful hue in the "foliage green" range. It is slightly more yellow in hue and deeper in mass tone, useful as a basic color and as a glaze with good lightfastness in the water vehicles. It contains phthalocyanine green and cadmium orange. A deep,
warm green traditional in the water color technique. The present, completely permanent, formulation replaces the traditional non-permanent one made with gamboge.

**Burnt Sienna:** Raw sienna which has been calcined or roasted in furnaces. Compared with the other earth colors, native or artificial, it has the most brilliant, clear, fiery, transparent undertone, and its red-brown top tone is least chalky in mixtures. Burnt Sienna is permanent.

**Burnt Umber:** Made by calcining raw umber. Compared with raw umber it is much warmer, being reddish rather than greenish in tone, darker, and somewhat more transparent. Otherwise the remarks under raw umber apply to it.

**Raw Sienna:** A native clay which contains iron and manganese. The best grades are from Italy. It is absolutely permanent. The color is similar to that of a dark ochre but warmer, more delicate, and transparent.

**Raw Umber:** A native earth. Its composition is similar to that of sienna but it contains more manganese. A dark brown, its tones vary from greenish or yellowish to violet-brown. It is not entirely opaque and absolutely permanent. Good grades are from Italy; the best grade (Turkey umber) comes from Cyprus.

**Payne's Gray:** Ivory black and ultramarine pigments. It appears a blue-black.

**Titanium White:** Titanium oxide, titanium dioxide. An extremely dense, powerful opaque white of high refractive index and great hiding power. It is absolutely inert, and permanent. Its properties have been known since 1870 or earlier, but was not successfully produced in a pure white grade until 1919 in Norway and America. 27

**Dyes:** A History of Dyeing

It is believed that dyeing was practiced as early as 3000 B.C. in China, although no conclusive proof of this is available. The earliest records of Indian religious and social practices belong to the period of about 2500 B.C.; they contain references to colored silk and gold brocades from which it can be concluded that dyeing was then already an established practice. It is believed that the craft was transmitted through Persia

to Egypt. Relics of ancient civilization have been preserved and more thoroughly explored in Egypt than in any other Eastern country. From paintings on the walls of tombs it can be inferred that as long ago as 3000 B.C. the Egyptians were making colored mats which they hung on their walls. It has also been established beyond doubt that Dyer's thistle, also known as Safflower, was in use in 2000 B.C. to produce red and yellow shades. By about 1450 B.C., the Egyptians were making textile materials of astonishingly delicate structure and were able to dye them in a whole range of different colors.

In the chronological sequence of history, classical civilization followed that of the Far and Middle East. Tyrian Purple, the badge of the patrician Roman, is believed to have originated in the Phoenician town of Tyre. We owe much of our knowledge of classical dyeing to the writings of Pliny, who has left a record of a number of recipes in use during his era. There was also a dyer's workshop excavated at Pompeii. The walls are decorated with a series of murals illustrating various operations as they were then performed.

In those days, dyeing was a profitable trade. With the collapse of the Roman Empire, the Dark Ages descended upon Europe. This period of history proffers limited records of the arts and crafts. It is not until 1371 that information about dyeing made its appearance again, when the dyers formed their own independent Guild in Florence. This Guild had only a short life, because it was dissolved in 1382, but soon afterwards, dyers' Guilds were to appear throughout all the European countries. In London, the first charter was bestowed upon the Worshipful Company of Dyers in 1471. As was the custom in those days, the Guild exercised a strict control over entry into the trade, the workmanship and the trading practices of its members.

Until the middle of the last century, all dyes were obtained from natural sources. Indigo, (extracted from the plant *Indigofera tinctoria*), and Alizarin, (obtained from the root of madder), have been used in India since the beginning of recorded history. Some of these products were probably exported to adjacent countries such as Iran (Persia), and may have spread from there to the Middle East. Neither alizarin nor indigo was available in Europe until the route to the East via the Cape of Good Hope had been opened up. *Carthamus tinctorius* or safflower, also known as Dyer's thistle, is a plant common in Asia, Africa and the Mediterranean
countries. The flowers contained a coloring principle which was used by dyers as a source of delicate rose and rich scarlet colors, and as a cosmetic when mixed with a talc. A textbook on dyeing and calico printing, written by Parnell in 1884, gives a good account of the natural dyestuffs which were in use before the advent of synthetic dyes.

We also know from Roman history that woad was used by ancient Britons. It was obtained from a plant known as *Isatis tinctoria*, which was cultivated in France, Germany, and in Britain. The active substance in the plant was indigotin, which was the same compound from which indigo was prepared in the East. Indigotin, blue in color, is virtually insoluble in water. Before it could be used as a dyestuff it had to be reduced. Until modern chemical reducing agents were available, dyers had to rely upon natural fermentation of vegetable matter; whereby hydrogen, a reducing agent, was produced. Woad contained the micro-organisms required to set up fermentation, which would bring about reduction of the indigotin. It was therefore only necessary to allow an aqueous infusion of the plant to stand under the right conditions, and in time, a liquor suitable to use for dyeing would be produced. It was, however, an extremely skillful operation to control the fermenting mass so that only the correct hydrogen-producing micro-organisms would flourish and multiply, and not become exterminated by some other species which had not the desired characteristics.

When the trade route to the East was opened up, in spite of much protest from the woad growers indigo soon replaced indigotin from all other sources. Woad was then only cultivated for its value as an ingredient to initiate fermentation of the indigo infusion. It is interesting to note that Tyrian purple has the same chemical structure as indigo, except that two hydrogen atoms have been substituted by bromine. Both of these coloring matters belong to a group which is now known as the vat dyes.

Most of the coloring matters of natural origin used in medieval times were not capable of producing permanent colors on textiles by themselves. The fibers had to be prepared for the reception of the dye impregnation with metallic oxides such as those of aluminum, iron, or tin. These substances were known as mordants, derived from the French word, *mordre*, which means to bite. The name was considered appropriate, because it was believed that the oxides bit the dye and held it on to the fiber. One of the most commonly used natural mordant dyes was alizarin, obtained
from the roots of the madder plant, which was cultivated extensively in Europe, the Near East, and India. It dyed a comparatively fast red color on an aluminum oxide mordant, and a purple-to-black shade with iron oxide. A variety of chocolate-colored tones were obtained by using mixed mordants of aluminum and iron oxides. Madder, cultivated in Turkey, yielded an exceptionally bright red; the name, Turkey red, came to be used as a general description of alizarin reds. The discovery of the Western Hemisphere and the opening up of shipping routes to the Americas brought fresh natural mordant dyes to the European market. Among these were Brazil wood, also known as Peach wood, which contained a water-soluble coloring matter producing red dyeings on an aluminum oxide mordant, brown shades on an iron oxide mordant, and rose-colored effects with tin peroxide. Haematoxylin, extracted from Logwood, found the most extensive application, and was used in great quantities for dyeing black on a chromium oxide mordant.

Cochineal came to the European dyers from Mexico, and was obtained from the female insect of the species, Coccus cacti. It dyed a crimson shade on an aluminum mordant, and was very similar to Kermes, which was extracted from an insect native to Spain. Cochineal formed a very fine crimson on an aluminum mordant, and scarlet on tin peroxide.

A limited number of inorganic pigments found a use in dyeing. A grass green was dyed by passing cloth first through a solution of chromium chloride and then through a solution of sodium arsenate. Chrome yellow, (lead chromate), was deposited in a comparatively permanent form on materials by passing it consecutively through solutions of lead acetate or nitrate, and potassium bichromate. A much longer description of the art of coloring textiles with natural dyes could be given, but the subject is only of historical interest here.

The year 1856 witnessed an event which was to bring about a fundamental change, not only in the practice of dyeing, but in the course of time, to the whole field of chemical industry. The new era was initiated by William Perkin, the son of a London builder, who was destined to follow in his father's footsteps. He was sent to the City of London School, which happened to be one of the very few which taught sciences in those days. His master noticed Perkin's aptitude for chemistry and appointed him as his assistant. Perkin's science master wanted him to go to the Royal College of Chemistry, which at that time was under the guidance
of the celebrated German chemist, Hoffman. Perkin's father wished his son to study architecture, and was greatly disappointed at the choice of chemistry as a career, but did not raise objections.

Perkin proved to be a promising student, and was kept so busy at the Royal College of Chemistry assisting Hoffman that he had no time to pursue his own research. He therefore set up a somewhat improvised laboratory in his own home, which he used during his holidays and in his spare evenings. Hoffman, in drawing attention to the desirability of producing quinine synthetically, established an objective which Perkin, at the age of 18, endeavored to achieve in his own laboratory. In the course of his experiments he oxidized aniline with potassium dichromate, and obtained a black precipitate. When this was extracted with ethyl alcohol, a brilliant purple solution was produced. All these experiments, which led to such momentous results, were carried out during the Easter vacation in 1856. Perkin's oxidation of aniline brought him no nearer to his main objective, namely the synthesis of quinine, but a few further experiments led him to conclude that he had produced a useful dyestuff. This work was of profound significance. It was the first time that a chemist had created a dye from comparatively simple organic molecules. It was also made from what was virtually a waste product in the destructive distillation of coal in the gasworks. The discovery eventually opened up an entirely new aspect of chemical industry.

Perkin sent a sample of his mauve dye to Pullar's of Perth, who tried it out in their works. It received a favorable appraisal with conditional stipulation that usage necessitated manufacture of the dye at an economic cost. Perkin, still only 18 years old, assisted by his father and his brother, built a factory at Greenford near London. Here he devised and erected a plant for nitrating benzene, a reaction which had never been carried out on an industrial scale before. He pioneered the large-scale reduction of nitrobenzene to aniline, and worked out a means of non-oxidizing the aniline and extracting the dyestuff. The greatest tribute is due to Perkin. He had the acumen, imagination and perserverance to establish a new industry, precededent by no previous experience.

Perkin's work fertilized the minds of organic chemists all over the world. If one dyestuff could be made synthetically, there was no reason why others should not be similarly produced. Since the original discovery, many thousands of dyestuffs have been synthesized in research laboratories,
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and from these between 1500 and 2000 have become successful commercial products. Perkin manufactured aniline on a commercial scale, and it was therefore natural that early applied research was directed principally towards dyestuff synthesis based upon aniline. 28

Dyes

Dyes are colored substances which are soluble, at least during some stage when applied to fibers. They owe their tinctorial power to certain chemical groups called chromophores which cause the dyestuff molecules to reflect specific light wavelengths. The dyestuff molecules also contain other chemical groups called auxochromes which govern the solubility of the molecule and help to fix it to the fiber. The lakes are insoluble colored compounds which, if not formed as a result of a chemical reaction in place on the fiber, are pulverised, mixed with an adhesive and painted or printed on to the fabric. When this is done, they are called pigments.

My interest is in the washing fastness of the colorants. This depends on the strength of attraction between the fibers and the colorant, which is called the affinity. If the affinity is strong, the fiber does not release the dye and its dyeing is fast. If it dissolves or is easily removed, the dye is said to bleed. A lake pigment which fails to adhere properly is said to crock.

These colors fall into three different classes. These classes are:

1. Those that depend on combining chemically with the fiber molecules.
2. Those whose solubility must be decreased and particular size increased after they have penetrated into the pores and crevasses of the fiber.
3. Those that depend on subsequent development of insoluble compounds within the pores and intermolecular spacings by first introducing a soluble color component followed by a substance that will combine chemically with it to form a precipitate.

The first group is found principally in the protein fibers wool and silk. These proteins are amphoteric, and according to their structures, have some free basic and some free acidic radicals located at intervals along the molecular chain. These sites permit acceptance of organic or other acids and organic or other bases. Thus, if the colorant or dye is acidic, it will unite with the basic site; if the dye is basic, it will

combine at the acidic site. This gives rise to two subclasses within the
first group.

The Acid Dyes

The acid dyes form most of the natural vegetable colorants and have
been popular for dyeing wool in the past. They are found in many plants
and come in many hues. Perhaps the most common are browns, tans, and
yellows. Their chemical composition is usually complex, but they will
generally react in a similar way to tannic acid, which has high affinity
for proteins and a powerful colloring effect. Each individual dyestuff,
however, requires careful processing to force it to react satisfactorily
with the fiber.

First the fiber must be wetted and swelled to a condition where the
pores and interior molecular spacings are opened enough to permit
penetration of the dye molecules. This is done by raising the temperature
of the dyebath and by stirring and agitating the fabric in it. When this
penetration begins to look satisfactory to the dyer, a setting agent such
as a stronger acid is added. In the setting operation, the acid causes
the weaker acid dye to collect into groups of molecules or micelles within
the pores. If the color is unevenly distributed, or is not to the required
depth value, a little detergent to assist penetration and levelling may be
added. When the dyeing is satisfactory, according to the test swatch or
fragment that has been dried, and the setting agent has been added, the
dye batch is drained quickly and rinsed in cooler water. The purpose of
this is to shrink the swollen fibers and hold the dye particles more
firmly in place. During this phase, acid rinse waters may be employed to
maintain setting conditions. This brief description may be altered
according to the individual dye and the whim or experience of the dyer,
but it does suggest principles of cleaning and procedures for handling an
acid dye problem.

The test for an acid dye should be made on all the hues in the
specimen to be cleaned. To test for bleeding, a small area of each
individual hue is wetted with a few drops of plain water. It is kept wet
for a short time, about one minute, and then a white blotter or folded
adsorbent tissue paper is applied to the area and pressed in contact for
a short time. It is then removed and examined for signs of color transfers
which, if present, warn the cleaner against wet cleaning. Next, a similar
small area of the particular color is wetted with a small amount of acetic
acid solution (about 2% CH₃COOH) and the examination with a blotter is repeated. If the color is not apparent at this point, the cause of the original color transfer may be to over-dyeing and failure to rinse the original dye job properly.

To confirm a suspicion that the dyestuff is of an acid class, another area is wetted with a solution of ammonium hydroxide (about 2% NH₄OH) which is applied as before, then examined. If bleeding occurs, the area is rewetted with the ammonium hydroxide, and acetic acid solution is applied generously and blotted again. If signs are absent, the dye class has been established. At this point, the effect of detergent solution (about 0.4% - 0.5%) with an equal amount of acid should be tried in the same way. If no bleeding occurs, the color may be wet cleaned. If bleeding is apparent, the color must be tested with drycleaning fluid in the same way to establish a method of cleaning safely.

Sometimes in case of doubt, it may be wise to try with hot wet cleaning solutions (60 to 70° C). Drycleaning fluids should not be used hot for several reasons.

As a summary acid dyes may bleed to alkalies, or detergents, especially if alkaline (soaps) are used about 60° C). They may be set by mild acids or sours.

**The Basic Dyes**

The basic dyes are less common among the natural dyestuffs but are apt to be found as synthetic colors on fabrics dating from the last half of the nineteenth century. Usually, when fairly new, they will be brilliant, but, because they are light sensitive, fading is likely to occur. They are also reputed to be less washfast, as a class, than the acid dyes. These basic dyes have an affinity for the occasional free acid sites on some of the amino-acids forming wool and silk (i.e. asparatic and glutamic acids). For this reason, they may be applied after an original dyeing with acid dyes to enhance the brightness of a particular hue. This is called top-dyeing and, when encountered, will add to the cleaner's problems.

Although alkalies will set basic dyes, acids will cause them to bleed. In this case, neutral washing conditions may be ineffective and the only way to remove soil may be to dryclean the object.

Basic dyes will also combine chemically with ligno-cellulose found in jute, bark, and wood products. This is because the lignins are made up of some phenolic type radicals which are faintly acidic in action and can
combine chemically with bases. These colors are used on jute cloth, and may be found on basketry and bark cloth. These dyeings are not very washfast, and bleed readily to detergent action.

The practical identification tests for the basic dyes follow a similar procedural pattern to that recommended for acid dyes. In this case, after seeing whether the test area has been over-dyed or not rinsed thoroughly, one may establish the class by testing with 2% acetic acid solution. At this point, excessive color transfer on blotting indicates presence of the basic dye. Confirmation is made by rewetting the spot with the acetic acid and applying a slight excess of 2% ammonium hydroxide or solution of some mildly alkaline salt. If the bleeding or transfer signs disappear on pressure blotting, the dye may be presumed to be a basic type. This test is not completely trustworthy because when the fabric or a particular embroidered area has been previously top-dyed, a considerable excess of the ammonium hydroxide may cause bleeding of the original acid dyeing.

Because many basic dyes are sensitive to acid-basic changes or the reverse, in a similar way to the familiar pH indicators, a decided color change phenomenon is also a weakness in some acid dyes. Another danger about testing with ammonium hydroxide is that the vegetable fibers, especially those containing ligno-cellulose, may produce a distinctly brownish color.

To summarize: in cleaning, basic dyes may solubilize or bleed in mild acids, probably will be solubilized by neutral detergents and will be set by mild alkalies.

Direct Cotton Dyes

The second principal dyeing mechanism grouping, that of the "direct cotton" or substantive class, is composed of colored substances that are appreciably non-ionizable, but soluble to a considerable degree. Many of these are salts of the acid dyes or related compounds. Coloring of the fiber depends on how well the molecules can penetrate into the fiber pores and eventually into the molecular spaces. This is one of the reasons why these dyes work quite well with cotton fibers, are less successful as a rule with flax, and may merely stain wool on the outside of the fiber with color that is readily dissolved.

For a fast dye job, the fiber is wetted, its pores and finer spaces expanded in the hot or boiling dye bath, and the dye solution forced in by working or stirring the fabric or fiber until a uniform acceptance occurs.
This is assisted by solubilizing and lubricating agents similar to detergents. As soon as satisfactory penetration is reached, the particle size is increased by addition of metallic salts either sodium chloride (NaCl or common table salt) or sodium sulphate (Na₂SO₄ or Glauber's salt). The effect of these salts is to cause the single molecules of dye to collect into micelles in a large number of molecules, forming particles of considerable size. By cooling the solution, draining, and rinsing in salt brine followed clear cold water, the fiber will shrink and entrap the dye particles. On drying, this seizure is reasonably secure. Like all dyeing procedures, this general scheme is subject to the whim of the dyer and the peculiarities of the dye.

A practical test for cleaning hazards, after learning whether or not the test area is over-dyed and affected by plain water alone, is to resaturate the spot with water, and then blot. If this is negative follow with a detergent solution, about 1/4% concentration, and after a few seconds, try blotting under pressure. Traces of color indicate a dye of this class. If the spot is resaturated with detergent, a salt brine solution of about 5% concentration may be applied and the area is blotted again. A lack of color transfer confirms the dye class. If this does not work, a more concentrated and colder solution may be required. Occasionally, on very heavily dyed goods, cleaning is only possible by drycleaning and before doing this, the color should be tested in a similar way with the several drycleaning liquids.

Mordanted and Developed Dyes

The third, or developed class of dyeings in which the soluble component of the dye penetrates the fiber and is fixed in place by a chemical reaction, may be expected to produce the best washing fastness. There are a number of modern ways of doing this dyeing, but perhaps a description of the two oldest methods will prove our point adequately.

The first method uses the mordanted dyes. In theory, it depends on setting up an anchor between the fiber chemical and the dyestuff molecule. The mordanting or anchoring agent must be able to attach itself to the fiber either by a chemical reaction with an active acid, or basic site, or a strong adhesive attraction to the fiber surface. The mordant must also be capable of developing active basic or acidic sites that are not attached to fibers, but which will react with an acid or basic dye to form the insoluble junction. By this mechanism, cotton cellulosic fibers may be
colored more or less permanently with acid or basic dyes, whereby normally only a stain would occur.

There are two types of mordants. The first type is used for setting an acid dye on cellulose. The best of which are the trivalent metallic hydroxides of aluminum, iron, or chromium. In general, the fabric is impregnated with a solution of a soluble salt of any of these, then steamed or boiled to hydrolyze the salt to the hydroxide which, in this condition, is gelatinous and sticky. The acid dye is then introduced and, as a result of chemical reaction, forms an insoluble colored mass. Chromium was not discovered until relatively recently so we would not expect it to be found in older textiles. Aluminum has been known and used for centuries as alum, and it produces excellent results. Iron mordanted dyes are common, deep and dull in hue, mainly blacks and browns. The trivalent iron, unfortunately, is a catalyst for eventual oxidation and these colors oxidize sooner than other hues. The salts of tin, the four valence metal are used to produce the so-called red or scarlet "bow" dyes. (An old English dyer's term for colors developed from dyeing in block tin vessels which probably was taken from the French word, beau.)

Tannic acid, a multivalent organic acid which may be hydrolyzed in place, is a useful mordanting agent for the basic dyes. In application, vegetable tannins from barks, fruits, or roots are extracted, and the solution impregnated into the fibers. These are steamed to produce a gelatinous acidic plating on, or within, the fiber pores. The basic dye is then precipitated on this bridge which, when dry, becomes quite insoluble. This dyeing technique produces dark but lightfast shades that also resist wash fading.

The vat dyes constitute the second class of developed dyes. The two best-known examples in historic textiles are indigo and Tyrian purple. When applied, these must be in the reduced or leuco state. At this time they are soluble under alkaline conditions, and they are straw or pale yellow in color. After penetration of the dyestuff, the fabric is exposed to the air for oxidation. As the oxidation develops, the hues change through green to blue indigo, or orange, then red, to deep crimson and purple for the Tyrian purple. As the color compounds oxidize, they become more and more insoluble and washfast. Likewise, the shades deepen as oxidation progresses.

There are no simple recognition texts for either the mordanted dyes
or the vat dyes, nor are any necessary in cleaning. Ordinarily they do not constitute a cleaning hazard, and the simple solubility tests for other types of dyes would reveal these colorants as safe.

**Paints and Prints**

A final test for painted, printed, or very deeply dyed fabrics is recommended. This is called a crocking test and is made by rubbing the color first with a dry white cloth or tissue, followed by rubbing with a damp one. If the white cloth or tissue shows a pick-up of color, crocking is indicated. It may be due to over dyeing or deterioration of the adhesive when pigments are used. In this case a similar test is made by rubbing the questionable color with a cloth dampened with dry solvent. This should ascertain whether drycleaning is feasible.

**Direct Dyes**

Until 1884 all the synthetic dyes which were produced had no affinity for cotton. They could only be applied after the fiber had been mordanted. This was a lengthy and complicated operation inappropriate for quick and economic dyeing of mass-produced cloth coming from the looms during the industrial revolution. In 1884, Bottiger prepared Congo Red and found that it would dye unmordanted cotton by the extremely simple process of merely boiling the material in a solution of the dye. The urgent need to simplify the dyeing of cotton was a great incentive to follow up Bottiger's work, and it was not long before an adequate range of analogous dyes became available.

These so-called direct dyes, which arose out of Bottiger's discovery, were extremely useful and still find very extensive application. Their weakness, however, is a lack of fastness to washing and other wet processes. Ever since 1884 there has been a constant search for a new means of producing colors on cotton which will stand up better to washing. The approach, until recently, has been to build up an insoluble color within the fiber by successive application of two soluble components capable of combining in the site. This idea was first given practical expression by A.G. Green, who synthesized a yellow direct dye, Primuline, which itself was of no importance because its fastness was very poor. It did, however, contain within its molecule, a primary amino group. Green

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demonstrated that it was possible to dye cotton with Primuline, causing it to react with nitric acid, and subsequently couple the diazotized product with beta naphthol to give a red dye of much greater wet-fastness. This principle has since been extended to quite a number of dyes and is still in use for blacks and navies where adequate fastness at a comparatively low cost is required.

The direct dyes, also known as the substantive colors, differ from the basic and acid dyes because cellulosic fibers have a strong affinity for them. Most of the colors belonging to this class are sulfonated azo compounds. A simple monazo dye is Diazamine Scarlet B (C.I. DIRECT RED 118), and the original Congo Red (C.I. DIRECT RED 28), was a disazo compound prepared by coupling benzidine diazotized at both amino groups with 2 molecules of maphthionic acid. Biazo Brown 3RNA.CF (C.I. DIRECT BROWN 138) is a trisazo direct dye of comparatively simple structure and polyazo or tetrakis azo member of the class is Chlorazol Brown GM (C.I. DIRECT BROWN 44). An important group of the direct dyes is those derived from stilbene, such as Diphenyl Chrysoine G (C.I. DIRECT YELLOW 19).

In 1887 Green prepared Primuline which was the first of the Thiazole direct dyes. The latest class to be added to the substantive dyes is those based on phthalocyanine. Durazol Blue 8G (C.I. DIRECT BLUE 86) is an extremely bright greenish blue with good light-fastness but poor wash-fastness. 30

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### TABLE 1. CLASSIFICATION OF DYES

<table>
<thead>
<tr>
<th>Dye</th>
<th>Characteristics</th>
<th>Fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid dyes (dye liquor is acidic)</td>
<td>Vary in fastness to light and washing. Bright colors</td>
<td>Wool, silk, nylon, acrylic, spandex</td>
</tr>
<tr>
<td>Azoic dyes, also called naphthol (devel-</td>
<td>Good fastness surpassed only by vat</td>
<td>Widely used on cotton prints. Polyester, acetate, olefin, rayon</td>
</tr>
<tr>
<td>oped on fiber). Insoluble color precipi-</td>
<td>dyes. Have tendency to crock</td>
<td></td>
</tr>
<tr>
<td>tates made by adding a solution of diazo compound to an alkaline solution of naphthol.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basic dyes (contain amino dyes).</td>
<td>Brilliant colors. Many are not fast to washing, light, or rubbing</td>
<td>Wool, silk, nylon, modacrylic</td>
</tr>
<tr>
<td>Cationic dyes—some as basic dyes</td>
<td>Wet fastness is excellent. Light fastness is fair to very good</td>
<td>Acrylics</td>
</tr>
<tr>
<td>Developed direct dyes (similar to direct cotton dyes, but must be developed on the fiber).</td>
<td>Good wash fastness. Fair light fastness</td>
<td>Cotton, rayon, silk, linen</td>
</tr>
<tr>
<td>Direct cotton dyes</td>
<td>Wide color range. No brilliant colors. Used where fastness is not necessary</td>
<td>Protein, cellulose</td>
</tr>
<tr>
<td>Disperse dyes, including insoluble azo, or anthraquinone dyes kept in colloidal suspension by sulfonated oils.</td>
<td>Good fastness to light, washing, and perspiration. Subject to fume fading</td>
<td>Acetate, nylon, acrylic, modacrylic, olefin</td>
</tr>
<tr>
<td>Fiber reactive dyes</td>
<td>Bright shades with excellent fastness</td>
<td>Cotton, linen, rayon, wool</td>
</tr>
<tr>
<td>Mordant and chrome dyes (can be made to combine with metallic salts)</td>
<td>Excellent fastness to wet processing and dyes</td>
<td>Wool, acrylic, cotton</td>
</tr>
<tr>
<td>Sulfur dyes (made by reaction of sulfur with organic compounds)</td>
<td>Wide range of rather dull colors. Fast to washing. Fair fastness to light</td>
<td>Cotton, rayon</td>
</tr>
<tr>
<td>Vat dyes: Pigments reduced to leuco compounds, which are soluble in alkali. Pigments are reoxidized by air or oxidizing agent.</td>
<td>Most satisfactory of all dyestuffs. Generally fast to light, washing, bleaching</td>
<td>Cotton, rayon, acrylic, modacrylic, nylon</td>
</tr>
</tbody>
</table>

### TABLE 2. TABULATION OF PROPERTIES OF DYE CLASSES

<table>
<thead>
<tr>
<th>CLASS</th>
<th>EXAMPLES</th>
<th>SUGGESTED TESTS</th>
<th>CLEANING PRECAUTIONS</th>
<th>SETTING AGENTS (suggestions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Turmeric, Annatto, Brazil wood</td>
<td>Try detergent with a little ammonia for bleeding evidence to pressure with blotter.</td>
<td>Avoid hot alkaline soaps. Watch prolonged soaking in neutral solutions.</td>
<td>Acetic or other mild acid, especially when rinsing.</td>
</tr>
<tr>
<td>Basic</td>
<td>Archil (Litmus), (Orseille), Persian Berry</td>
<td>Try a neutral detergent first, followed by acetic acid for evidence of bleeding to pressure on a blotter.</td>
<td>May withstand very short exposure to mild alkalies. Avoid mild or strong acids. Be wary of even moderate exposure to neutral detergents.</td>
<td>Very weak ammonia solutions, especially if quite cold.</td>
</tr>
<tr>
<td>Direct Cotton</td>
<td>Lo Kao (Chinese green), Saffron, Safflower</td>
<td>Try hot water or soap solutions for evidence of bleeding on a blotter</td>
<td>Avoid long periods of soaking in hot soap suds or alkaline detergents.</td>
<td>Salt brine followed by cold water.</td>
</tr>
<tr>
<td>Mordant</td>
<td>Cochineal, Lac, Logwood, Weld, Kermes, Madder (Turkey Red), Safflower, Annatto, Safflower</td>
<td>Try in turn suggested tests for acid, basic and direct groups. If negative, dye is probably mordant. Do not be fooled by color changes.</td>
<td>No special warnings necessary except in the case of “Turkey Red” which may bleed in drycleaning.</td>
<td>Cold water alum.</td>
</tr>
</tbody>
</table>
CHAPTER II

BASIC PRINCIPLES OF TEXTILE CLEANING

In the conservation of artistic and historic textiles, cleaning to some degree is almost always necessary. This work should not be attempted, however, without a knowledge of the risks involved in all the possible treatments.

1. What kinds of soils are encountered in the textile?
2. Which cleansing medium is safest and most effective?
3. What additives and cleaning aids are required?
4. What working temperatures will be best, considering the soils and fabric condition?
5. What sort of mechanical action may be used safely?
6. How long may the specimen remain exposed to the cleansing medium?
7. How should the spent cleansing mixture be replaced or removed, number and time of rinses, removal of rinse solution, method of drying?
8. How to finish with after-treatments?

How Various Soils Affect Cleaning

There may be ways of classifying soils. For example, we might do so according to origin, or to the way they are deposited. Thus, they may be airborne, water deposited, contact smeared, accidental, the results of oxidation or chemical degradation of any of the textile components: fibers, dyes, textile finishing agents, adhesives, preservatives and other treatments. Alternatively, they may be fragments from wear, abrasion and bacterial, fungal or insect damage. A practical way of grouping soils, as done by the professional cleaner, is to divide them into types that will yield, in general, to the three main cleansing mediums: air, water, and organic liquids.

Air Removable Soils

These are usually loosely attached deposits of sand, dust, other earthy matter, lint or fiber fragments and finely divided foreign trash. They may be airborne, contact smeared, or, less often, water deposited.
To get rid of them, we depend mainly on an air blast accompanied by shaking, agitation, scraping, brushing or other more or less violent mechanical actions which break up and dislodge the foreign substance. The air has very little actual cleansing power other than its ability to pick up and carry away particles or droplets of the soil, through the fundamental application of jet power: either vacuuming or direct air blasting. With an air blast, it is possible to add scouring materials such as sand in sand blasting, or sawdust in fur cleaning. Collection of spent scouring substances and dust becomes a problem, whereas a vacuum nozzle not only produces a jet action on the soil but also takes care of dust collection.

Vacuum cleaning is a valuable first step in most cleaning processes, because often loosely encrusted soil matter will disintegrate on wetting, either by water or other solvents, and redeposit as finely divided particles which subsequently may become much harder to remove.

Wetcleanable Soils

Soils that respond to cleaning in water are designated as wetcleanable. The following eight categories differ chiefly in the cleaning aids that may be needed for the job.

1. Soils that are soluble in water alone
2. Those that require alkaline conditions for removal
3. Those that may be released best by acids
4. Substances that will require digestion by enzymes
5. Stains that can be bleached or oxidized
6. Stains that can be decolored by reduction
7. Substances that may be dissolved by sequestrants or chelating agents;
8. Insoluble deposits that may be emulsified or solubilized by detergents.

Soils That May Dissolve in Water Alone

Although plain water is a most versatile solvent and will dissolve a great many substances, its action is sometimes so slow and limited that it must be aided. There are a number of things it will dissolve readily. Some notable classes are: simple inorganic salts, especially those of the alkali metals, potassium, sodium and ammonium; a number of salts of other metals, the hydroxides of the alkali metals and a few hydroxides of their metals; many oxygen containing organics of low molecular weights, among them alcohols, organic acids, sugars and numerous crystalline compounds.

The amount of any substance that water will hold in solution in most cases depends on the temperature. The speed of dissolving also
depends on how near it is to saturation with respect to the particular solute. The temperature rule of greater solubility in hot water does not hold for gases, and a very few other substances, notably calcium sulfate \((\text{CaSO}_4)\) which is more soluble in cold water.  

**Why is Water Such a Good Cleaning Medium?**

Water is the best known and most widely used of the fluid cleaning systems; it is probable that many of us never stop to think about the unique chemical and physical properties that make it such a good cleaning agent. We may not know why it fails under the conditions in which it comes to us. The purpose of this discussion is to describe how, by the help of additives, temperature controls, mechanical manipulations and special treatments, its effectiveness can be increased and its deficiencies overcome.

Water has been called the universal solvent and for this reason is the most useful cleaning fluid. Because it is such a good solvent, it is likely to be contaminated with dissolved substances and undesirable suspended matter. However, if filtered and free of bacteria or fungae, and chemicals such as strong acids, strong alkalies, iron salts and chlorides, it will probably be suitable and safe for most textile cleaning.

**What Happens When Water Dissolves Most Inorganic Substances?**

Water is a remarkable liquid because not only will it dissolve organic substances such as sugars, starches, gelatins, colored stains and dyes, it also has the peculiar power of causing many inorganic chemicals to split up into electrically charged particles. These are called ions and are either negative or positive. The process is called ionization.

When ionized, chemical compounds are able to exchange ions freely, which on collision form new substances. If these happen to be insoluble in water or if soluble and do not re-ionize after joining, the products may be removed from the action scene. Water is one of the very few chemicals that has ionization powers. In many instances, success in cleaning depends on our management of the behavior of a number of the different ions so a brief presentation of ways of controlling them is made at this time.

**Can Water Itself be Ionized?**

Water is a simple chemical compound, being composed of two atoms of hydrogen combined with one atom of oxygen, empirically represented by the

---

formula \( H_2O \). Structurally, we write it as \( HOH \). The reason for this last abbreviation is that unless a great deal of energy is expended, water does not break down into elements hydrogen and oxygen but will itself ionize to a very limited extent into hydrogen ions (\( H^+ \)) and hydroxyl ions (\( OH^- \)): 

\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- .
\]

Thus the chemical formula \( HOH \) is most representative of these two special ions, both of which have a very great influence on cleaning. As a rule, the hydrogen ion retards soil and stain removal, whereas the hydroxyl ion favors cleaning.

**What is an Acid? An Alkalie?**

Absolutely pure water contains only one free hydrogen ion and one free hydroxyl ion in ten million molecules of the liquid. At this point it is neutral. Substances that will increase the concentration of hydrogen ions when dissolved in water are acids. Other substances that increase the concentration of hydroxyl ions are called bases or alkalies, the latter being defined as water soluble bases.

**What is Neutralization?**

Acids and alkalies are opposing classes of chemical compounds and when their solutions are brought together, will form water and a salt. 

\[
\text{ionize} \quad \text{Salt} \quad \text{ionize} \\
\text{HCl} + \text{NaOH (in water)} \rightarrow \text{H}^+ \text{OH}^- + \text{Na}^+ \text{Cl}^- \quad \text{HOH} \quad \text{and} \quad \text{NaCl} .
\]

When the resulting solution is balanced at the neutral point of water mentioned above, we say that the solution has been neutralized.

**What is the pH System of Describing Acidity or Alkalinity?**

In a widely used numerical comparison system of describing the degree of acidity, called \( pH \), the neutral point is given the value of \( pH \) 7. In this system \( pH \) 0 is most acid and \( pH \) 14 is least acid or most alkaline. A \( pH \) chart indicating the more important properties of water at various degrees of acidity, as far as textile cleaning is concerned, is shown by Table 3 and 4. Note that the safety zone for textile cleaning ranges from an acidity of about \( pH \) 4 to an alkalinity of about \( pH \) 10. Except for unusual soil or stain conditions, we should maintain our cleaning solutions within these limits. ²

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### TABLE 3. PH VALUES OF SOME COMMON ACIDS AND ALKALIES*

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>pH at 0.1% concentration</th>
<th>pH at 10% concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>12.3</td>
<td>13.3</td>
</tr>
<tr>
<td>Sodium orthosilicate</td>
<td>Na₂SiO₃</td>
<td>11.2</td>
<td>12.1</td>
</tr>
<tr>
<td>Sodium sesquisilicate</td>
<td></td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>Sodium metasilicate</td>
<td>Na₂SiO₄</td>
<td>11.4</td>
<td></td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>11.2</td>
<td>12.1</td>
</tr>
<tr>
<td>Trisodium phosphate</td>
<td>Na₃PO₄·12HOH</td>
<td>11.1</td>
<td>11.9</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>NH₄OH</td>
<td>8.6</td>
<td>9.1</td>
</tr>
<tr>
<td>Modified soda</td>
<td>(Na₂CO₃</td>
<td>10.3</td>
<td>10.3</td>
</tr>
<tr>
<td>Neatral soap</td>
<td></td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Borax</td>
<td>Na₂B₄O₇</td>
<td>9.2</td>
<td>9.2</td>
</tr>
<tr>
<td>Phenolphalein changes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>NaHCO₃</td>
<td>8.3</td>
<td>8.3</td>
</tr>
<tr>
<td>Boric acid</td>
<td>H₃BO₃</td>
<td>5.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>H₂CO₃</td>
<td>4.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH</td>
<td>3.4</td>
<td>3.8</td>
</tr>
<tr>
<td>Methyl orange changes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCOOH</td>
<td>2.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>HF</td>
<td>2.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>(COOH)₂</td>
<td>1.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>1.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>

*PH determinations above 10 are somewhat approximate in the first decimal place, due mainly to the effect of sodium ions on glass electrode measurements. The above pH values, with the exception of those of the silicates and of soap, have been calculated from data found in chemical literature.

### TABLE 4. A PH CHART

- **Most alkaline**: pH 14
- **Strong alkalies**: pH 13
- **Ammonia†**: pH 11
- **True soaps 'poly-phosphate builders'**: pH 10
- **Weak alkalies**: pH 9
- **Pure water neutral**: pH 7
- **Weak acids 'sours'**: pH 6, 5, 4
- **Acetic acid†**: pH 3
- **Strong acids**: pH 2, 1
- **Most acid**: pH 0

Removal range for oxidised paints and also oils and for animal glues

This area is usually safe for treating most fabrics

- Removal range for rust, corrosion, starches and paste adhesives

| Wool and other proteins may be damaged* |
| Cottons and other cellulosics may be damaged* |

†Removal range for oxidised paints and also oils and for animal glues

*The extent and seriousness of the damage will depend on the condition and age of the fibres, the time of contact and the temperature of the solution.

†These pH values are for concentrations of about 0.1%, or less. Both ammonia and acetic acid are volatile and will disappear in a short time, usually before the fabric is damaged.

Why Are Wash Water Solutions Made Alkaline?

Because most soils and natural stains are acidic, washing solutions as counteractants must usually be alkaline. Thus alkalies in some form are added. This is also necessary, because soft water is often acidic and cleaning is much better under alkaline conditions. At this point control of pH becomes necessary and how pH may be regulated becomes important.

Obviously a very few drops of an acid or alkali would produce a minimum change. A larger quantity would increase or decrease the pH, as the case may be. This is not satisfactory, because of difficulties in determining the precise amounts to be added.

What Are Strong Acids? Why Avoid Them?

Fortunately, not all substances ionize to the same extent when dissolved in water. In the case of the acids, three-hydrochloric, sulfuric and nitric- will ionize completely. These are called strong acids because a very small amount will produce a pH approaching the maximum acidity point of zero (0). Most of the other acids, which we will call weak, will ionize only partially. The extent of ionization of the weak acids will vary with the particular compound, and its concentration in the solution. An example of this is acetic acid, the sour principle of vinegar, which at 0.1% produces a pH of about 3 and does not change appreciably when the concentration is increased ten times. The acetic acid dissolves completely but only a small part ionizes, leaving a reservoir of unionized but readily available acid in solution.

What are Strong Alkalies? Why Avoid Them?

There are a few strong alkalies, namely sodium hydroxide and potassium hydroxide. These ionize completely and approach pH 14 when a little is dissolved in water. The remainder are weak. A classic example of which is ammonium hyroxide (aqua ammonia) which at 0.1% concentration produces a pH of about 9, but does not change greatly on adding more. Both acetic acid and ammonium hydroxide are popular cleaning reagents because they are volatile and, on evaporating, do not concentrate on the fabric. Consequently, the pH or OH or H+ ion-effects cannot become damaging on drying the material. 3

How May Excessive Alkalinity or Acidity Be Controlled?

Where it becomes necessary to provide permanent acidity or alkalinity

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3Ibid.
at a specified pH in a textile, or an even more closely controlled pH condition in a solution, we may resort to the use of "buffering" type chemicals, known as soap builders and Laundry sours. The builders are alkali forming salts, while the sours are acid forming salts.

What Is A Salt?

In order to explain how these chemicals work, it will be necessary for us to recall that when acids and alkalis are mixed in solution in the proper proportions, neutralization results and a salt and water are formed. By evaporating the water, we can separate the salt in its crystalline or solid form.

What Is Hydrolysis?

In the opposite case, when the salt is dissolved in water, the process is called hydrolysis. The salt forms negative and positive ions which are in motion and which on collision will unite briefly but immediately re-ionize.

Where the salt is the result of the union of a strong acid and a strong alkali, as for example common salt or, chemically speaking, sodium chloride, it will split up into sodium ions and chlorine ions as illustrated by the chemical equation: NaCl + HOH → Na⁺ (ions) + Cl⁻ (ions) + HOH (substantially unionized) and since the positive and negative ions are equal the solution is neutral.

How Do The Builders Work?

The alkaline salts or builders are the result of the chemical union of a strong alkali and a weak acid. In this case, the salt in solution ionizes incompletely. The weak acid ions capture, on collision, some of the hydrogen ions furnished by the water and in doing so allow the corresponding hydroxyl ions from the water to remain free. This unbalances the neutrality in favor of alkalinity and the pH registers above the neutral point pH 7. As these hydroxyl ions are used up, more can be furnish by the water and the pH level will remain constant.

How Do The Sours Work?

The acids producing salts are formed by a combination of a weak alkali and a strong acid, such as hydrochloric, sulfuric or nitric acids. In the same fashion as just explained, the weak metallic ion of an acid forming salt captures a hydroxyl ion from the water and thus frees a hydrogen ion. The number of these is limited, but the pH is unbalanced below the neutral point of pH 7. When used, their replacement follows the
same pattern as explained previously.

Without the hydrolysis theory mechanism, we would have great difficulty in controlling soil removal and dye losses in cleaning.

Three rules that may be helpful aids in selecting acid forming and alkali forming salts:
1. Strong acids and strong alkalies form neutral salts.
2. A salt of a strong acid and a weak alkali is acidic.
3. A salt of a strong alkali and a weak acid is alkaline.

**What is Hard Water?**

Before the advent and widespread availability of modern synthetic detergents, soft water was a necessity for good textile washing results. Where the water was hard, a great deal of trouble was taken to soften it.

Hard water may be defined as water that contains dissolved salts of metals, principally calcium, magnesium and iron. These hardness forming chemicals are picked up by the water as it flows through the ground and combine chemically with true soaps to form insoluble sticky soap curds which have no cleaning properties and deposit out on the work to produce an undesirable graying of the fabric.

Formerly, many solutions for cleaning called for rain water or distilled water, both of which are condensed from water vapor and, in doing so, leave the objectionable non-volatile hardness salts behind. Because rain water is usually not dependable nor plentiful in many temperate regions and distillation is an expensive process, many users of large quantities of soft water now employ surface ion exchange principles for water softening. In this case, the hard water is passed through a bed of granules of zeolite, a natural mineral, or one of the more recently developed synthetic resin granules with increased surface ion acceptance and exchange abilities.

The zeolites or resins are complex insoluble chemicals which have the peculiar power of adsorbing certain ions (i.e. sodium), onto their surfaces. They also have an attraction for other ions such as calcium, magnesium, ferrous iron, and others, providing the concentration of these hardness substances in the water is greater than that of any of the sodium ions present in the solution. In this case, an exchange takes place and the hardness ions deposit on the resin, releasing sodium ions which are non-hardness forming because they make soluble soaps and not the soap curds.

If water, containing a high concentration of sodium ions such as in
strong salt brine, is passed through the zeolite bed, the exchange is reversed and the mineral or resin can be rejuvenated. The effluent in this case contains the hardness ions and is run to the sewer for disposal.

The development of synthetic resins for ion exchange has brought about treatments that can produce contamination free water which is not possible in distillation, and will be satisfactory for almost all washing purposes.

What Is The Principle Of Complex Ion Formation?

Complex ion formation by sequestrants or chelating agents is another popular modern way of removing undesirable ions from washing waters. The sequestrating agents are chemical compounds that are already composed of a complex ion which has a peculiar power of exchanging non-hardness forming ions from within the ionic structure for one of the common hardness producing ions, for example, the action of sodium hexametaphosphate on soluble calcium salts:

\[ 2\text{CaSO}_4 + \text{Na}_2(\text{Na}_4\text{P}_3) \rightarrow \text{Na}_2\text{SO}_4 + \text{Na}_2(\text{Ca}_2(\text{P}_3) \]  

water complex soft complex ion hardness ion water containing soluble calcium

This same chemical sequestrant is also capable of exchanging sodium ions for calcium in precipitated soap curds and is one way to brighten textiles grayed in previous cleanings.

In other instances, the chelating agent reacts directly with the unwanted ion to form a complex molecule which may or may not be soluble but which does not permit it to react with any other ion. Modern physiology chemistry is full of illustrations to support this. One of the most spectacular being the control of ferric iron poisoning by desferrioxamine B, a long chain molecule that is supposed to entwine itself around the ferric atom and prevent it from reacting. In the reduced state as ferrous ions, the sequestration may be accomplished by citric acid, oxalic acid, hydrofluoric acid or Calgon \(^4\), but some of these might not be tolerated within the living body. as such, and thus might be toxic themselves.

What Other Troublesome Ions Are Sometimes Encountered?

Other ions that might be considered as unwelcome in water for washing purposes are chlorides, nitrates, sulfides and, on occasion, copper or ...

\(^4\)signifies trade-marked product.
other rare metals from saline lakes, wells, springs, and industrial wastes. Any of these may be removed by distillation, chelation or by surface active resin treatments. In each case, the nuisance must be diagnosed and the most effective treatment prescribed.

How Do We Usually Get Rid of Suspended Matter, (Muddy Water)?

Suspended matter is ordinarily cleared by coagulation with a flocculation agent such as an aluminum salt, either alum or aluminum chloride. This causes emulsified micelles in suspension to coagulate into particle sizes that can be removed by sand filters. Any free aluminum ions, if the water is aerated, will form aluminum hydroxide. This is insoluble and forms a gel which will settle out on standing. The resulting water is slightly acid and contains either hydrochloric acid or sulfuric acid. As a rule, the acid concentration is so dilute that it may be neglected. But if it is a factor of danger in a process, these acids may be removed by filtering through a specially chosen surface resin bed.

What May Be One of the Faults of Rain Water?

Aeriated and rain waters, especially if cold, are apt to contain dissolved oxygen and other atmospheric contaminants. It is possible that these may have damaging effects on some textiles, especially if they have already been oxidized in aging. Usually most of the dissolved oxygen and acid gases can be removed by boiling the water before use. 5

Soils That Respond to Alkaline Cleaning Agents

Most soils encountered are those that require alkaline additives to water for best cleaning. Many of the natural products of oxidation are acidic. Often these are not soluble until they are changed by neutralization into salts or soaps or other compounds of the alkali metals that compose most of the basic substances used. Study and experience with detergency has shown that cleaning and emulsification are usually faster and more efficient under alkaline conditions.

Some of the more common acidic soils are substances of edible oils and fatty foods, perspiration and body contact smears, matter condensed from smoke and air fumes, fruit and plant juices, many vegetable and synthetic dyestuffs, and products of decay of vegetable and animal matter. Protein matter such as glues and blood stains, while they may not be acidic, may be attached and depolymerized by alkalies or strongly basic

5Ibid, pp. 17-22
chemical agents.

The ionic activity of the usual wetcleaning solution has much to do with its effectiveness. As a rule, cleaning is best above pH 10 and decreases markedly as the pH drops to neutrality or below. This high pH may have no serious damaging influence on cellulosic fibers, but, with protein fibers, degradation is likely. For this reason, control of the pH within reasonable limits is advisable and a buffering system necessary. At the same time there must be a source of strong positive ions that will form soluble products upon reaction with otherwise insoluble acidic soils. This is the reason why the alkali metals are chosen. The hydroxides of these metals are so completely ionized that pH control is not practical when they are used alone, so alkaline salts are used to bring about a buffering or alkalinity control action.

These alkaline salts are salts of a weak acid and a strong base, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). When dissolved in water, these dissociate completely, i.e., NaOH $\rightarrow$ Na$^+$ + $\cdot$OH, and the only way that the number of destructive hydroxyl ions ($\cdot$OH) can be controlled is by drastic dilution. At 0.1% concentration this alkali has been reported to have a pH of about 12.3, far above the protein danger point.

Ammonium hydroxide (NH$_4$OH) is a weak alkali that ionizes incompletely, thus, NH$_4$OH $\rightarrow$ NH$_4^+$ + $\cdot$OH + (NH$_4$OH) (dissolved molecules). At 0.1% concentration it has a pH of about 8.6, and at 1.0% about pH 9.1. At high concentration, about 28%, it does not exceed pH 11.5. This alkali is volatile and often escapes long before damaging effects are noticed.

An alkaline salt such as borax produces a pH of 9.2 at both 0.1% and 1% concentrations. The control is based on the theory that water is ionizable to an extremely limited extent and that when a salt of a strong alkali and a weak acid is dissolved, a series of reactions take place. This produces a limited number of free metal ions and free hydroxyl ions.

The following is an example of this process:

\[
\text{Na (CH}_3\text{COO) + HOH} \rightarrow \text{Na}^+ + \text{OH} + \text{HCH}_3\text{COO} + \text{Na(CH}_3\text{COO)}
\]

6 These reaction equations are only illustrative for the composition of the solutions, and are not quantitative.
Since many of the weak acids do not ionize to the same extent, it is possible to choose an alkaline salt that will produce a reasonably limited pH range, even though the concentration is not adjusted precisely.

Those alkaline salts are sometimes called soap builders because they are frequently added to soaps or washing mixtures which increase the cleaning powers, especially for very heavily soiled cotton fabrics. Compounds such as trisodium phosphate (Na$_3$P$_4$O$_7$) sodium metasilicate (Na$_2$SiO$_3$) and sodium carbonate (Na$_2$CO$_3$) are representatives of builders. At a recommended concentration of 0.1% they produce pH values of 11 - 12 and are too active for safe wool cleaning work, especially under hot water conditions.

Neutral soaps at concentrations of 0.2%, give a pH of about 10. The best cleaning is achieved at about pH 10.5, so the soap is usually made with a builder which prevents the formation of fatty acids that may interfere with its work.

Synthetic detergents, on the other hand, are said to work best at about pH 9.5, and for these, a class of complex phosphate ion compounds called polyphosphates are reputed to be valuable additives. Two of these, tetrasodium pyrophosphate (Na$_4$P$_2$O$_7$), and tripolyphosphate (Na$_3$P$_3$O$_10$), may be encountered in heavy duty home washing powders. Although unlikely to attack wool proteins chemically, they may cause some shrinkage and cause dye bleeding in high concentrations. For these reasons they should not be used without testing.

Other very weak alkaline salts i.e., borax (Na$_2$B$_4$O$_7$) and sodium bicarbonate (NaHCO$_3$), have very little neutralizing power but may have special uses. The borax is used for scouring soap curd deposits from utensils and for heavy grease and oils. The sodium bicarbonate or baking soda is sometimes mixed with sodium carbonate or washing soda, half of each by weight, to make "modified soda". This has a buffered pH of about 10 which does not vary appreciably when the concentration is increased.

Characteristics of Soils That Respond to Acids

As a general definition, a strong acid is one that ionizes completely. There are three: i.e., hydrochloric acid (HCl), nitric acid (HNO$_3$) and sulfuric acid (H$_2$SO$_4$). All other acids are considered weak although they vary greatly in strength or completeness of ionization.

Metal corrosion products such as iron rust, cooper, and other metallic oxides are examples of soil substances that may yield to acid
treatments. Direct chemical union with the oxide, to form a soluble salt of the metal, will require a particular acid, e.g., hydrochloric acid (HCl) would be suitable for dissolving iron rust on wool, but would not dissolve silver. Since it is one of the three strong acids, it would damage soiled cotton, and would not be suitable for silk. Earthy matter such as lime, chalk or cement may be dissolved by acids but again a specific acid must be chosen.

A few colors, notably the basic dyestuff class, and some organic chemicals, are soluble in acidic solutions. Nylon fiber is affected by the strong acids at about 5% concentration. It will also dissolve in concentrated formic acid, but this is probably an individual property of that particular chemical. As another example, concentrated acetic acid (above 30%) will dissolve cellulose acetate.

Acids are often necessary for setting acid type dyes and for neutralizing residual alkninity in the washing process. To avoid damage to cotton fibers, either mild acids or buffering salts, which will produce a pH level of 2.5 or above, are recommended.

Acetic acids (CH₃COOH), the sour principle of vinegar, is the most widely used of the true acids. At concentrations of approximately 1% its pH is about 2.8. At 28% concentration, its pH is 2.0, but because it is volatile, it will usually evaporate before damaging cellulose. Formic acid (HCOOH), found in bee and ant venom, is sometimes substituted for acetic acid where a slightly stronger acid is needed; it is also volatile. Hydrofluoric acid (HF) is a third volatile acid which is even stronger. It is a valuable rust remover but will attack glass and metals, so it must be used in wooden or plastic basins.

For permanent setting of acid dyes, and preventing the development of brown discolorations in cotton or linen goods when dried slowly, the cleaner can use acid producing salts known as laundry sours. The safest of these are sodium and zinc silicofluorides (Na₂SiF₆, Zn Si F₆) sometimes known as fluosilicates. When dissolved in water, they produce a limited number of free hydrogen ions (H⁺). They produce a buffered pH of 3 to 4, even quite concentrated and are not apt to damage cellulose. Of the two laundry sours mentioned, the zinc compound is preferred because it is more soluble than the sodium compound. If not rinsed away, it provides protection against moth damage in wool.
Soils That Are Affected by Sequestrants

Certain special soils, e.g., soap curds, which are formed by hard water, are dissolved readily by polyphosphate sequestrants such as a tetrasodium pyrophosphate and tripolyphosphate. These were mentioned previously in the discussion of alkali builders for synthetic detergents. A near relative of these, sodium hexametaphosphate \( (\text{Na}_6\text{(P}_3\text{O}_9)\text{)} \) is an exceptionally efficient, practically neutral reagent for this purpose. These substances are known as complex ion compounds and have the peculiar property of substituting sodium from the complex ion for calcium, magnesium, ferrous iron and other bivalent metals. The following equation illustrates this mechanism:

\[
\text{Na}_2\text{Na}_4\text{(P}_3\text{O}_9)\text{6} + 2\text{Ca}^{++} \rightarrow \text{Na}_2\text{Ca}_2\text{(P}_3\text{O}_9)\text{6} + 4\text{Na}^+ .
\]

Complex ion Calcium sequestered

It is probable that hydrofluoric acid acts a similar way when removing rust. Oxalic acid \( (\text{H}_2\text{C}_2\text{O}_4) \), which is substituted for the hydrofluoric acid when a fabric contains metallic or glass yarns, probably owes its ability to remove rust to sequestering or chelating action.

Other examples of complex ion formation are found in the use of potassium cyanide for silver stain removal. This cyanide is a violently poisonous substance, and fortunately it is seldom necessary to use it. Silver stains may be removed by first treating them with iodine and then dissolving the silver iodide in sodium thiosulphate. This substitute treatment may bleach some dyes so it must be done with care and the excess iodine removed at once. Copper corrosion may be removed by ammonia and certain amines. The principle of this action is again formation of complex ions.

Soils That May Require Digestion by Enzymes

Substances such as protein deposits, including blood stains, body stains, body decomposition matter, gelatin, food stuffs of many sorts, starches, sugars and other soils, can be degraded or hydrolyzed by enzymatic action. Such organic catalysts are quite effective for removal of glues, sizings, pastes and natural adhesives that may have hardened and have become objectionable from aging processes.

These enzymes or digesters are effective in action but require neutral pH conditions and tepid temperatures, not exceeding about 45°C. Below about 30°C the conversion becomes very slow. In digesting, the soils must remain in contact with the solution, and the temperature maintained
constant for about half an hour. The timing is left to the operator's discretion and his experience.

Although digestion is a very gentle process, it has been known to weaken and attack wool that has been previously damaged by repeated oxidation and other drastic chemical action. From this, one may suppose that both old wool and old cotton might possibly be affected, to some degree, by this soil removal method.

Colored Stains That May Respond to Reduction

Bleaching is often considered to be the removal or the changing of an objectionable, foreign color in a textile to an acceptable hue. This general definition would include oxidation, reduction and hue change phenomena such as blueing or brightness changes with modern fluorescent dyes. Specifically, however, bleaching is destructive of the color by oxidation, which may be defined simply as adding oxygen to a compound. Cleaners prefer to think of bleaching as controlled oxidation.

Reduction is the opposite of oxidation and may be defined as the removal of oxygen. In cleaning this is called stripping, which denotes controlled reduction.

There are two main classes of objectionable colored soil substances. One of these is metal corrosion which is sometimes intensely colored and insoluble. These corrosion soils are the result of oxidation, and as a rule they will respond to reduction where by the color changes to a lighter, different hue and often become soluble. Iron and manganese are two examples of metals that will corrode in this way.

The second stain class is made up of organic substances that are either true dyes or natural color substances related to them. Each contains certain chemical groupings in its molecular structure, called chromophores, which are arranged in regular, repeating sequences. Chromophores have more or less unstable double or triple bonds between carbon or nitrogen atoms. These bonds are readily attacked and changed by oxidation or reduction. Reduction of a chromophore is considered less drastic than oxidation because it is not likely to completely sever chromophoric double bonds such as \( \text{C–C} \) or \( \text{N–N} \), but may change them to \( \text{C=C} \) or \( \text{N=N} \). They cease to be color forming, but by mild oxidation may return to a double bond formation later.

Reduction is endothermic and requires continued application of heat. Since it is the opposite action of oxidation, we may consider it as an
unnatural process, but one which may be useful in inhibiting or repairing oxidation after bleaching. If not stopped at a precise stage, bleaching may go too far and damage the fiber. Secondly, many dyes and stains will respond to reduction but may not be removed by oxidation. The vat dyes are of this nature.

The professional cleaner has three types of reducing agents at his command. First, for bleaching control, sodium bisulfite (NaHSO₃) is a popular agent. It is not a powerful dye stripper, however, and for that purpose, most professionals prefer either sodium hydrosulfite (Na₂S₂O₄) or formaldehyde sulfoxalate (NaHSO₂·CH₂O·2H₂O). When stripping a garment, for example, a solution of approximately 2% is heated to about 50°C and then the garment immersed. The temperature is maintained for about half an hour. If at that time the color intensity has not been lowered, a fresh solution is made up, the garment entered, the temperature raised 10°C and the reducing action continued. This sequence may be repeated if not at first successful.

Spot bleaching with hydrosulfite stripper is sometimes done, by wetting the spot in question with detergent, and then sifting on some of the powdered chemical. A little 5% solution of acetic acid applied to the spot and worked in with a wooden or bone spatula hastens the chemical action. Steam will also help. In addition, this is a way of testing a dyed area to see if it may be reduced by the reagent.

The hydrosulfite strippers should not be used in steel or metal vessels. Stoneware, unscarred enamelware, glass or wooden vessels are preferred. Articles containing silver, copper, iron, or other embroidery and buttons will be tarnished by the hydrosulfites and under these circumstances black stains may develop. However, these stains will usually yield to dilute hydrofluoric acid.

The titanium strippers constitute another type of reducing agent that is popular with professional cleaners. These are titanous chlorides or sulfates (TiCl₃ or Ti₂(SO₄)₃) and are purple liquids. In action, they are oxidized to four-valent substances. One of these is titanium oxides (TiO₂), a white but insoluble residue. This will respond to dilute hydrofluoric acid (HF), as will titanous hydroxide (Ti(OH)₃), a yellow precipitate sometimes formed by accident when ammonium hydroxide is applied. These insoluble compounds may be rendered colorless and soluble by dilute hydrofluoric acid. When using this acid, fabrics should be rinsed
thoroughly and the use of glass or enamel utensils or table tops avoided. The titanium strippers are more efficient if hot.

Colored Stains That May Respond to Oxidation

Stains that respond to oxidation are common, but this type of bleaching of historic textiles should always be considered as a last resort treatment. Two general classes of oxidizable stains may be mentioned. First, there are those that are the result of displacement of dyes within the textile itself, or perhaps of accidental contact with another colored specimen at some stage of cleaning or wetting. These are called bleeding or smear stains. Sometimes they will respond to soaking without a bleach being used. In this event, the solution temperature, the time of treatment, the additives, such as alkalies or acids, the detergents and perhaps special dyesetting agents are important, and present a unique problem. All of these items have to be determined by tests and observations. Often, however, the soaking technique will not remove all traces of the stain, necessitating bleaching.

The second main type of bleachable stains covers those that are either the result of accidents or develop, from oxidation or aging processes, within the textile itself. The accidental stains may be from spills of various foods or beverages, or contact with wet vegetation. Those that develop from within the textile itself may come from the breakdown of the fiber, perhaps from oxidation of a colorant, or from a finishing agent such as starch. As a rule many of these, regardless of source, appear as tan or browned rings or spots. If the history of the specimen were known exactly, the original cause might be traced to wetting with a natural sugar or starch that had not been removed completely at the time of the accident. As these carbohydrates age, they oxidize through various stages to develop into compounds resembling acid dyes. These have no particular affinity for cellulose unless mordanted, but combine with proteins to make a very "fast" stain on the original, neglected spot. This theory will account for the gradual yellowing of cottons or linens over the years.

If hot, slightly alkaline solutions (pH 10, 60°C) do not remove the stain substance from cellulosic fibers, bleaching with a "chlorine bleach" will often restore satisfactory whiteness. This does not guarantee that the brown color will not return. The protein fibers are damaged or destroyed by chlorine bleaches. Sugar oxidation products form very insoluble substances with these proteins, so other types of bleaches have
not proved to be satisfactory. Drastic oxidation is necessary and the other bleaches may not have the specific whitening action attributed to the chlorine type.

There are two general classes of bleach widely used in the cleaning industry. The chlorine bleaches are commonly used in laundering cotton and linen goods because they are inexpensive and do a good job. The peroxides are used principally for wool and silk, but, occasionally, they may be selected for delicate cotton specimens.

The chlorine bleaches are actually hypochlorites (\(^{\text{–}0\text{Cl}}\)). When these come in contact with the fiber surfaces, they decompose to produce nascent oxygen (\(0\)), which is very reactive. If not in contact with the fiber, the nascent oxygen forms molecular oxygen (\(O_2\)), less efficient for oxidation purposes.

The hypochlorite radical is obtainable in three, widely marketed, chemical compounds: sodium hypochlorite \((\text{NaOCl})\) a liquid of about 5 1/4% concentration for household use; calcium hypochlorite or H.T.H. \((\text{Ca(OCl)}_2)\) a crystalline powder, only slightly soluble; and calcium oxychloride, or bleaching powder \((\text{CaOCl}_2)\) still less soluble. In most cases these last two are converted to soluble \(\text{NaOCl}\) before use, by reacting them with sodium carbonate \((\text{Na}_2\text{CO}_3)\), thus:

\[
\text{Ca(OCl)}_2 + \text{Na}_2\text{CO}_3 \rightarrow 2\text{NaOCl} + \text{CaCO}_3
\]

The \(\text{CaCO}_3\) precipitates and settles and the liquid is decanted off. When used in a bath, the concentration should be diluted to about 1/10% or even 1/50% for very old specimens. Best bleaching conditions are slightly alkaline - pH 10 - in warm water. Thorough rinsing followed by a mild acid to neutralize the alkali is advisable.

Spot bleaching for small areas may be done with 1/2% or lower concentrations in warm water. In this case, a cotton-tipped wooden applicator is saturated with the bleach and applied to the stain. The stain is observed, and when the color is lessened to the desired degree, a reducing agent such as sodium bisulfite \((\text{NaHSO}_3)\) is applied at about 2% concentration, with another wooden cotton-tipped applicator. This is followed by rinsing and adsorbing the excess moisture by blotters.

The peroxide bleaches are suitable for bleaching on wool or silk because, unlike chlorine types, they are not so likely to cause yellow discolorations and fiber damage. Two substances that fall into this class
are widely recommended. These are hydrogen peroxide (H₂O₂) and sodium perborate (NaBO₂·3H₂O·H₂O₂). Hydrogen peroxide is supposed to break down on contact with the fiber surface, according to the chemical equation:

\[ \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O} \text{ (nascent oxygen)} \]

It is a very weak acid and is stable only when kept under acid conditions. When made alkaline, as with ammonium hydroxide, it decomposes rapidly according to the above equation. Exposure to light or heating will also cause decomposition of the acidified hydrogen peroxide. These chemical properties provide us with methods for controlling it in bleaching. We may also stop its action by antioxidants such as sodium bisulfite. Immediate decomposition is also catalysed by metals, especially iron, and for this reason, metal vessels or table tops should be avoided when bleaching. Because of this property, it may be used as a rough qualitative test for blood spots. If the unknown dark spot foams rapidly when a drop of hydrogen peroxide is applied, it is probably blood.

Although peroxide can be purchased in several concentrations, 3%, 10%, 30% or even higher, the 3% or drug grade is preferred from a fire hazard standpoint in storage or handling. In bath bleaching, it is usually diluted down to 0.2 - 0.5% concentration, depending on the problem. For spot bleaching, where it is under visual observation, about 1% may be tried. The bleach is applied first, then often followed by dilute ammonium hydroxide to speed up the action.

Sodium perborate is the second member of the peroxide bleaches that is widely used for protein fiber bleaching. When dissolved in water, the crystal molecule is supposed to undergo a chemical change:

\[ \text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2 \text{ in solution} \rightarrow \text{NaBO}_2 + \text{H}_2\text{O}_2, \text{ producing sodium metaborate and hydrogen peroxide.} \]

This reaction is catalyzed on contact with the fabric and fibers. Since granular sodium perborate is of only slight solubility, about 3 1/2% at 20 - 30°C, this limits the maximum concentration of H₂O₂ to less than 0.7%. This precludes the danger of getting too high a concentration, even when an error is made in mixing. At temperatures above 50°C, approximately, the solution or moist granules decomposes spontaneously, producing molecular oxygen gas; moderate temperatures should be maintained. This decomposition effect, however, is sometimes employed by professional cleaners in spot bleaching, wherein the small area is covered by perborate granules, then heat and moisture are applied by a gentle steam jet. This is a rapid but wasteful method, quite possibly too drastic a procedure
for use on old, weak fibers.  

Soils That May Yield to Organic Solvents

There are many soils that do not dissolve or soften appreciably in water, but may be attacked by non-aqueous liquids. Familiar soils of this type are oils, greases, waxes, tars, resins, some adhesives, rubbers, certain gums and lacs, varnishes, paints, modern polymers, and plastics. Many of the natural fats and oils can be saponified by alkalies in water solutions, or emulsified by soaps and detergents. Often it is more efficient, and safer to clean them in one of the modern drycleaning solvents. There are some substances mentioned above that may not dissolve in the special drycleaning fluids but can be attacked by special solvents.

Petroleum Solvents

Two classes of special drycleaning liquids have been developed and are in widespread use for commercial cleaning. One of these is composed of selected fractions obtained in distillation and cracking of crude mineral oils or petroleum. A great deal of care is taken to obtain a solvent that does not volatize appreciably at temperatures below 60°C (140°F). This precaution is necessary so that explosive mixtures of the vapors and air cannot occur except at extreme and unbearable temperatures. This particular grade is known as 140°F flash solvent. Flash point solvent has been approved for use in homes by many states and municipalities in the USA as being a safe drycleaning solvent. Another similar product, having a flash point of 38°C (100°F), is Stoddard solvent.

Both of these are excellent cleaners for most textiles and will remove many common soils, especially greasy, sooty matter. Avoid their usage on dyes that are oil mordanted colors, similar to wax crayons, as they will dissolve. Soils resembling sugars, salt, and other water soluble deposits may be removed by emulsifying a little more water into the solvent than ordinarily present. The emulsifying agent is a special type of detergent called a drycleaning soap and is used in small quantities, no more than 4% at most. The mixture of water-drycleaning, soap-drycleaning solvent is called a "charged" system and its use has improved drycleaning performance greatly.

These petroleum solvents are inexpensive, of low toxicity, and have

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no damaging effects on most textiles; therefore they are very widely used by cleaners in the USA. They will swell and weaken rubbers, many paints and some plastic substances, and should not be used on printed goods or paintings without testing. Although they are flammable and will burn if temperatures exceed the flash point, they are very much safer than automobile gasolines or commercial napthas.

**Synthetic Solvents**

The synthetic or man-made solvents constitute the second main group of the drycleaning liquids. Most of these are chlorinated hydrocarbons, although in recent years, fluorinated hydrocarbon (non-flammable) solvents are used for professional cleaning, in locations where fire regulations will not permit the petroleum types. In general, they are more rapid in cleaning action than the petroleum solvents, and will attack some soils and substances that do not yield to that group.

These chlorinated hydrocarbons are rated as poisonous, but toxicity varies greatly from one compound to another in degree and effect. Likewise, some persons are more resistant to the toxicity than others. To support these statements, the poisonous effects of two similar solvents, carbon tetrachloride (CCl₄) and perchlorethylene (C₂C₄) are quite different.

Carbon tetrachloride is a dangerous and violent poison. When its vapors are breathed, not only does it act as an anaesthetic, but the vapors may also damage body organs. This last effect is cumulative, and each succeeding dose renders the victim less able to withstand further damage. The liquid may also be adsorbed through the skin with similar results.

By comparison, perchlorethylene is rated according to industrial safety codes as about 1/20 to 1/2 as toxic as carbon tetrachloride. Its effect is said to be intoxicating chiefly, and the dangers of accumulating serious organic damage is less. Because there have been many deaths attributed to carbon tetrachloride, it is seldom used or approved for garment cleaning presently. Instead, perchlorethylene is very widely used in the USA for the purpose, and although thousands of people are exposed to its fumes daily, authentic reports of serious poisoning from it are very rare.

In Europe, a near relative, trichlorethylene (C₂HCl₃) has been more widely used because it was more readily available and less expensive than C₂Cl₄. Recent advances in chemical engineering technology, however, have
lowered the costs of perchlorethylene and it is becoming more popular. Trichlorethylene is rated as slightly more toxic than perchlorethylene and has the additional drawback of being more likely to bleed some modern dyes, especially when there is a temperature increase, as with the cleaning process. Losses from evaporation are also slightly greater.

These two chlorinated solvents are efficient cleaners, both from the point of view of special solvent action, and of insoluble soil particle removal. This last property may be due to their high specific gravities, approximately 1 1/2 times that of water or nearly twice that of the petroleum solvents. This makes them more buoyant, and the greater weight of fluid produces a more concentrated mechanical action in stirring or tumbling, for disintegrating soil masses.

Like the petroleum solvents, these synthetics require a drycleaning-detergent-water "charge" for salt and stain removal. They are about five times as costly as petroleum solvents and the fumes are toxic. They must be contained in closed machines, their vapors condensed wherever possible, and the condensate returned to the system for re-use.

Fire and explosion hazards are non-existent. In case of fire on the premises, however, the hot vapors may decompose into noxious products, one of which is phosgene (COCl₂), a very poisonous gas. Water in contact with some of the chlorinated types, especially in the light, cause them to break down into hydrochloric acid (HCl) and other products. The acid is not soluble in the solvent and may be separated by filtering through cotton or woolen rags. This is the usual practice in conventional drycleaning procedures. The acid may also be neutralized by an alkali. Again, decantation or treatment by rag filters may be needed for removing the moisture.

In addition to the drycleaning fluids previously discussed, there are a number of organic liquids that have special solvent power for particular substances, especially soils that do not yield to wetcleaning or ordinary drycleaning. Among these are soils that result from either accidental or intended polymerization of more or less readily combined molecules. Chemical actions such as oxidation, reduction, hydration, dehydration, heating or cooling may cause single molecules to form giant molecules. As a rule, these very large molecules are less soluble in ordinary solvents than smaller molecules. Occasionally, certain solvents are compatible with and can penetrate the polymer. The original soil
substance molecule will be an unsaturated compound so that cross linking can take place. In many cases, the degree of setting or polymerization increases with time; thus, an aged deposit is often harder to break down and remove. Vulcanized natural rubber is an exception because oxidation contributes to its depolymerization and breakdown.

There are three major groups of soils that may yield to special solvents but not to water or ordinary drycleaning solvents. First, there are the unsaturated oils occurring in paints, foods, atmospheric smogs, soots and other greasy deposits. The saturated oils are readily soluble in drycleaning solvents, but if ignited or heated, may crack into unsaturated fractions. These, in turn, are susceptible to repolymerization or drying, as in paint film development. The natural; unsaturated oils such as linseed and soya bean oils are notorious in this respect. When relatively fresh, these paint films can be liquified and removed by drycleaning solvents, but as they adsorb oxygen from the air they harden and are less easily penetrated. At this stage, aromatic hydrocarbon solvents such as benzene \((C_6H_6)\) toluene \((C_6H_5CH_3)\) or xylene \((C_6H_4(CH_3)_2)\) may attack the film. All three are toxic, flammable and readily form explosive mixtures with the air. Benzene is reputed to have the highest solvent power, toxicity and flammability, toluene is less so and xylene is the mildest. None of the three is likely to damage natural textiles or dyes, but any prints or painted specimens must be regarded as risks and the solvents should be tested carefully on them before general application.

Adhesives used for reinforcement and mending of old textiles are a second, and less frequent type of soil. Usually these are glues that may be attacked by wet processing with acids, alkalies, or digesters. Occasionally shellacs, gums and resins, that do not respond to wet processing may be found. Many of these are alcohol soluble. Either concentrated ethyl alcohol or methyl alcohol may be effective. Complete rinsing is necessary, because, if diluted with water, the adhesive may deposit back on the fiber. The alcohol solution is not soluble in petroleum solvents and only slightly soluble in the synthetic drycleaners. Some dyes are dissolved in the alcohols so the conservator should test all colors involved with the solvent before using.

Rubber and rubber latex adhesives are commonly used for adhering reinforcements to backs of old rugs. Very often these must be removed
for cleaning and repairs. Frequently they will soften or dissolve in one of the aromatic hydrocarbons mentioned above under "drying" oils. If the rubber has been vulcanized or polymerized with sulfur, it may resist these solvents, and in such instances carbon disulfide (CS₂) a very poisonous, inflammable and foul smelling substance, will often dissolve or soften the rubber. Where softening only is desired, the drycleaning solvents will usually suffice.

Other commonly encountered adhesives, such as cellulose nitrate or cellulose acetate cements, that are insoluble in water, drycleaning solvents and even the aromatic solvents, will dissolve in acetone (CH₃COCH₃), ethyl acetate (CH₃COOC₂H₅) or perhaps amyl acetate (CH₃COOC₅H₁₁) or other ketons and esters. Most of these are flammable and toxic to varying degrees. Of these several solvents, only pure amyl acetate is safe for use on cellulose mono- or sequiacetate fiber. The others will dissolve it.

The lacquers, special paints, and many unknown insoluble polymerized deposits, that do not respond on testing to the conventional wet or drycleaning solvents, will sometimes soften to a point where they may be scraped from the textile by gentle manipulation with spatulas or other tools. If such deposits do not dissolve appreciably, they may swell and disintegrate. Some synthetic rubbers, especially chloroprene, silicones, new kinds of paints and fiber protective treatments, may be of this type. If none of the special solvents mentioned above prove helpful, as a last resort one may try one of the special paint removers often called paint strippers. These are mixtures of many of the solvents already named, perhaps with other additives such as methylene chloride, formic acid, and special detergents and solubilizers to enable them to penetrate a massive deposit, break it up, and emulsify it in a solvent liquid. Some of the ingredients of these mixtures will dissolve or disintegrate cellulose acetate, nylon and other synthetic fibers, so thorough testing prior to use is advised. The principles of penetration by which these strippers work is explained in the next section. ⁸

Insoluble Soils

Soils that are insoluble in either wet or dry solvents often respond to emulsification by surface active agents. Soaps and other detergents belong to this class of chemicals and the soils they attack best are crusts

⁸Ibid., pp. 49-53.
of earthy materials, partly polymerized sticky airborne deposits like soot, smears deposited under contact pressure, and very finely divided particles from solvent born slurries and suspensions, e.g. muddy water. Of all of these, the finely divided particles seem to be the hardest to dislodge because, due to their minute size, they will penetrate all crevices, as well as deposit on the rough surfaces of the natural fibers. Once these submicroscopic, but insoluble particles, have been deposited, the attraction between the fiber surfaces and the particles becomes very great, and it is only by overcoming this surface attraction that removal can be accomplished. At this point, the surface activity agents or surfactants are needed.

**Surfactants**

When a surfactant works on an adsorbed surface-bound particle, a number of things happen. First, the surface tension, or the attraction between molecules, of the cleansing medium is decreased. This permits the liquid to approach the substrate, or fiber, and the soil particle more closely. This is called wetting. The second stage of the process takes place when the surfactant molecules are aligned in such a way that one end joins the substrate while the other end extends into the cleansing medium, forming an imaginary furry effect.

To visualize this clearly, one should recall the structural formula of a soap, e.g. sodium laurate (C\(_{11}\)H\(_{23}\)COONa) the chief ingredient of coconut oil soap. This molecule is composed of a moderately long chain of CH\(_2\) groups connected to a carboxyl and solubilizing metal grouping COONa:

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COONa}
\]

The long carbon atom chain is attracted to most surface substances, especially the fibers, and is compatible with oily matter. According to the same theory, the water-attracting group, -COONa, is repelled by the surface, thus causing the molecule to point away. This water-attracting end of the molecule is known as the hydrophilic group, the other end is referred to as the hydrophobic part.

When the surfactant molecule is quite short, it functions as a wetting agent, only because moisture is already very close to the surface being cleaned. This does not mean that it is a good detergent, although wetting is one of the necessary attributes of a good cleaning agent. A longer chain, however, might be able to penetrate the interface between a soil particle and the fiber surface, causing a separation. This would
help to release the soil from the surface and is probably what happens during the second stage of cleaning. Figure 6

The third step of the detergents process is penetrating the soil mass, which we may suppose to be porous. The attraction forces of the hydrophobic ends of the surfactant molecules enable the molecules to be adsorbed in any surface pores or cracks in the soil mass. At the same time, the hydrophilic ends attract water into these spaces, and produces a swelling force, if aided by mechanical action, this swelling force helps to break up the soil mass into minute particles, which are theoretically surrounded by layers of oriented surfactant molecules. (Figure 7) This is referred to as emulsification or peptization, depending on whether the soil mass is liquid or solid. These individual particles are very large when compared to molecules, and unless collision is prevented, a gel or collection of particles may occur, there redepositing the soil substance. Figure 8

At this point in the process, it becomes necessary to maintain separation or suspension of the particles, at least until they can be removed from contact with the substrate. Mechanical disturbance, jet action or heat will do this, but the soil-bearing emulsion must be taken away as soon as possible, lest coagulation and redeposition should occur. One way to prevent or delay this danger is to select a detergent of suitable molecular structure and characteristics. This detergent molecule must have a relatively rigid, chainlike structure, as illustrated by the chemical formula for the coconut oil soap mentioned earlier. At the same time, the molecule must bear a strong electrical charge on the hydrophilic end. It should be soluble to a limited extent, but should be only weakly ionized, if at all. When such a molecule orients itself to the soil fragment, the electrically active parts extend out and provide the particle with a charged surface, which when in the vicinity of a similar particle, will cause a mutually repelling action. This helps to maintain suspension within the cleaning medium. Figure 9

The length of the hydrophobic chain affects the suspension powers of the detergent molecule. A longer structure appears to produce more buoyancy of soil particles as well as more protection from accidental collision. The larger and longer molecules, however, unless modified by the presence within the chain of hydrophilic groups or radicals, such as \(-\text{CH}-\text{CH}_, \text{CH}_2\text{OCH}_2_, \text{CH}_2\text{O}, \text{CH}_2\text{OH}, \text{COOH}, \text{NH}_-,\) and other combinations, are less soluble in water than shorter surfactant molecules.
Figure 6

A porous soil particle adheres to the surface. Surfactant molecules from the detergent solution penetrate the area of adhesion and orient themselves on surfaces. Section of (b) surfactant molecules from the detergent solution enter pores and orient themselves on surfaces.

Figure 7. Attraction of water (0) to the hydrophilic ends of the surfactant molecules (0) results in swelling of the pores and disintegration and fragmentation of the soil.

Figure 8. Disintegration completed; separated particles form a jelly or cream-like emulsion. Van der Waal's effect no longer holds.

Figure 9. Electrostatic repulsion.

From this argument, a general rule as to the effect of the length of the molecule may be set up. Those shorter than 10 carbon atoms may be soluble in cold water, but are not especially good cleaners. At about 20 carbon atoms in length, unless modified as noted above, the compounds are usually so slightly soluble, even in very hot water, that they fail as cleaners but may be very good lubricants. The short-chain molecules are useful wetting agents and emulsifiers for gels and creams.

Some textiles because of their very fragile condition, cannot stand mechanical agitation or handling, especially when wet. In these cases, one may try soaking techniques employing a solubilizing agent. **Solubilization** is a phenomenon midway between that of dissolving a substance to form a molecular dispersion and that of emulsification or suspension of larger particles. During attack by a substance appreciably soluble both in an encrusted soil and water, a complex of a single molecule of soil, plus one or more molecules of the solubilizing agent, and numerous molecules of water is formed. This grouping or micelle is relatively small. It is easily distributed into the surrounding water because it approaches molecular distribution conditions. A continuing attack of this sort eventually disintegrates the soil deposit into an almost clear mixture with the cleansing medium. Figure 10

Many detergents and soaps possess this valuable property, some more than others for specific soils. For this reason, a knowledge of the probable composition of the soil would enable one to select a compatible surfactant. The effectiveness and speed of penetration and solubilization also depend on the temperature, the pH and its concentration, which in this case may be lower than when emulsification is desired. The importance of lather or foam on a cleaning solution is that it indicates a satisfactory concentration of detergent micelles in the cleansing medium. Although some authorities mention the floating power of stable suds for light soil particles such as fiber fragments and surface deposits of dye crusts, this contributes very little to the overall cleaning job. When the lather is fine and stable, however, the detergent and water mixture is usually in the best condition for emulsification and suspension of the soil. Lack of satisfactory suds or a sudden change indicates poor cleaning conditions. This may be due to acidity or temperature changes, addition of salt or overworking the solution mechanically.

Excessive suds sometimes may be a nuisance and for gentle soaking a
minimum of lather may be best. This indicates a favorable proportion of single detergent molecules, rather than collected micelles in the cleansing mixture.

Lubrication is often mentioned as a desirable characteristic of a detergent, and may be described as that property of a detergent that enables it to spread over surfaces and form a protective film of appreciable depth. If this film sticks tenaciously to the surface, and is thick enough to overcome the Van der Waal's effect of attraction of like molecules when brought very close together, then soil is unlikely to redeposit. For this reason, detergents with long molecules make the best lubricants.

Figure 10

The solubilization process. Chemical formulae and explanatory text, as given in this figure.


Why is Limited Solubility Necessary in a Detergent?

Solubility may be defined as mixing of molecules of one substance, a solute, in another, a solvent. In the most simple case, the molecules are singly dispersed throughout the mixture which is called a solution. However, we may also have a colloidal solution which is a stable distribution of micelles within the mixture. As a rule, small molecules

9 Ibid., pp. 53-57.
are more easily dispersed in the solution than large molecules. The smaller molecules do not collect into micelles readily and as these are necessary to a certain extent for good cleaning, especially where insoluble soil is concerned, we choose an agent that is not too soluble so that these micelles may be able to form. On the other hand, if the surfactant molecule is too large, not enough single molecules will be available to engender wetting, penetration, and protective spreading.

**What Are Some of the Things That Affect the Solubility of the Detergents?**

The shape of the detergent molecule and the attraction dissimilarity of the ends has been already discussed. Other influencing characteristics of these molecules are:

1. The chain length is important. If less than 10 carbon atoms long, it may be too soluble to form useful micelles. If more than 18 carbon atoms long, the substance is, unless chemically modified in some other way, too long and large to be soluble at reasonable working temperatures.

<table>
<thead>
<tr>
<th>Carbon atoms</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>in cold water</td>
</tr>
<tr>
<td>10</td>
<td>cool water</td>
</tr>
<tr>
<td>12</td>
<td>tepid water</td>
</tr>
<tr>
<td>14</td>
<td>120°F</td>
</tr>
<tr>
<td>16</td>
<td>140°F</td>
</tr>
<tr>
<td>18</td>
<td>160°F</td>
</tr>
<tr>
<td>20</td>
<td>insoluble in 200°F</td>
</tr>
</tbody>
</table>

2. The above generality about the length of chain does hold good for unsaturated molecules where there are double bonds between one or more pairs of carbon atoms. In this case, an unsaturated chain detergent is more soluble than a similar saturated chain compound.

3. Some detergents have even longer molecules than the 18 carbon stearate used as illustrations. In this case, the continuity of chain is interrupted at intervals by oxygen or some hydrophilic group. 10

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Types of Detergent

Colloidal chemistry studies over the past fifty years have shown that detergents, or substances that help cleaning through surface activity principles, may be divided into three main groups, according to their behavior in an electric cell.

According to their ionic activity in solution, these three groups are:

1. **Anionic detergents** in which the hydrophilic end of the molecule is positive. A solution of an anionic detergent in an electrolytic cell will deposit a slimy coating on the anode or positive pole. Figure 11

2. **Cationic detergents**, wherein the hydrophilic end bears a negative charge which will produce a similar effect on the cathode or negative electric pole of an electrolytic cell. Figure 12

3. **Nonionic detergents** bear no electrical charges and form no deposits because of the electrophoresis effect and both electrodes of the cell will remain clean. Figure 13

Anionic Detergents

The anionic types are the most widely used in cleaning. Structurally, these consist of a moderately long hydrophobic carbon atom chain joined to a hydrophilic group bearing a strong positive electrical charge. For simplicity, these molecules are often represented thus: $\text{-}_\text{0}^+\text{0}$; where the hydrophobic end is shown as a line bearing the negative charge and the hydrophilic end is represented by 0, the symbol for oxygen, and bears a positive charge indicating a strong basic element.

Hundreds of individual anionic compounds have been studied and patented, but for our purpose, two main subgroups are recognized. We designate these soaps and synthetic detergents or syndets. 11

What Are Soaps?

In practice, **soaps** are formed whenever animal or vegetable fats and soils are brought together with a soluble base or alkali. This is the basis for soap manufacture and also is the reason why either ammonia or washing soda are so effective for cleaning greasy articles. In one case, the soap is made to be used later and is usually purified and refined while in the other event, the soap formed merely assists in the cleaning effect at the scene of cleaning action.

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Figure 11. Action of anionic detergents in an electrolytic cell.

Figure 12. Action of a cationic detergent in an electrolytic cell.

Figure 13. Non-ionic detergent molecules are not affected by electrical currents.

The natural animal or vegetable fats are compounds of glycerine and fatty acids and in soap manufacture glycerine is a valuable by-product which is separated and recovered. This does not happen when the soap is made as a step in cleaning. Actually, the soap is a chemical compound resulting from reacting a fatty acid with an alkali.

Fatty acids are long chain (10-18 Cs) hydrocarbons usually ending with the organic acid group \[\text{C}_n\text{O}^--\text{OH}\]. The fatty acid \[\text{COOH}\] is not soluble in water but will dissolve in many drycleaning solvents. When a fatty acid combines chemically with alkalis such as potassium; sodium and ammonium hydroxides and some of the organic bases related to ammonium, water soluble soaps result. Chemists call this particular reaction Saponification. These several metallic ions bear strong positive electrical charges and in consequence confer anionic properties to the molecule in addition to water solubility. Thus schematically the fatty acid \[\text{COOH}\] in contact with \[\text{NaOH}\] (sodium hydroxide, a very common alkali) produces by saponification \[\text{COONa}^+\] or simply \[\text{O}^-\text{Na}^+\] (anionic detergent). 12

Soaps may be defined as esters or salts of fatty acids and metallic hydroxides of strong bases. The true soaps are soluble in water. Because very few bases, other than the alkali metals sodium and potassium, and the strong organic bases ammonia and ethanol amines, donate sufficient solubility, their number is limited. This is especially true because the length of the fatty acid carbon chain is also limited to between 12 and 18 atoms unless modified.

The metallic soaps, which comprise compounds of other metals with fatty acids are nuisances if formed in the cleaning process.

The cleansing soaps have several defects. They react with calcium, magnesium and iron ions in hard water to foam soap curds, which are sticky gel-like masses that deposit out on fabrics or washing equipment. This not only reduces the useful soap concentration but adds to the insoluble soil problem. It is one of the reasons why soft water is needed for cleaning. Soaps are decomposed by acids into salts and free fatty acids, thus:

\[
\text{C}_{11}\text{H}_{23}\text{COONa} + \text{HCl} = \text{NaCl} + \text{C}_{11}\text{H}_{23}\text{COOH}
\]

<table>
<thead>
<tr>
<th>Soap</th>
<th>Mineral Salt</th>
<th>Insoluble acid</th>
<th>Insoluble fatty acid</th>
</tr>
</thead>
</table>

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The fatty acid has no cleaning action in water.

Soaps coagulate in salt brine, and if the brine is concentrated enough, will precipitate out. This is the way that soap is separated from solution when it is manufactured. It also verifies the fact that soaps do not work in sea water.

Neutral or built soaps, which may be necessary for removing residual acidity in a textile, may be alkaline enough to promote shrinkage or even felting in wool. Superfatted soaps that are incompletely saponified are usually safe in this respect, but may not provide the best cleaning. They are excellent lubricants, however, and for that reason are employed in leather cleaning.

Unless made from highly purified fatty acids, ordinary soaps are obtained from natural oils and fats, and thus are seldom composed of precise chemical constituents. These natural fats are usually mixtures of glycerides of many different saturated and unsaturated fatty acids, so that soaps of exact chemical compositions are rare. However, if a soap is decomposed into its fatty acids and then these are dried and melted, we can accurately measure a solidifying or melting point of the mixture.

This temperature when reported in degrees Celsius is called the titer. As a practical rule, the best working temperature for a soap solution is about 12-14°C above its titer. Because the titer is indicative of the solubility of the soap, we often hear the terms high titer used for a hot water soap, medium titer for a warm water soap, and low titer for a tepid water soap. Very few soaps are efficient in cold water.

The particular alkali that makes up the soap will also affect its solubility. Sodium soaps are least soluble, potassium soaps more so, and ammonium soaps still more readily dissolved. Additionally, solubility is dependent upon whether the principal fatty acids in the soap are saturated or unsaturated chains. These chains form the more soluble soaps. This is the reason why Castile soap, which contains a large percentage of oleic acid ($C_{17}H_{33}COOH$), an unsaturated fatty acid from olive oil, dissolves in tepid or even cool water. A soap made from beef or mutton tallow, which is mainly the saturated fatty acid ($C_{17}H_{35}COOH$) does not dissolve satisfactorily until the water temperature is about 70°C. One should note that the two fatty acids are the same carbon atom chain length.

For washing woolens, Castile soap might be an excellent product were it not for the fact that when the oleate oxidizes in aging, peroxides
are formed across the weak double bond. These are supposed to continue oxidation which form vile smelling aldehydes.

True soaps may be decomposed by biological processes and are unlikely to poison beneficial bacteria in sewerage disposal systems and streams.

The high titer soaps are rated as very efficient cleaning agents, when used in hot water and rinsed thoroughly at high temperatures. Synthetic detergents compete with moderate and low titer soaps especially for cleaning wools, and in some cases are considered more satisfactory.

**Synthetic Detergents**

Because the anionic syndets can, by controlled planning and manufacture, be produced so as to avoid many of the defects of soaps, they are displacing the fatty acid compounds for general cleaning usage. For example, the chemical composition can be restricted to uniform products that are more soluble than soap and will work better at lower temperatures. They can also clean satisfactorily at pH levels below the felting or damage points of wool. These anionic detergents may be affected by calcium, magnesium or iron in hard water, but because the resulting precipitates are not sticky curds or slimes, their deposits are much less noticeable than those of soaps. Salt brines also have less drastic coagulation effects on this class. In fact, in some cases, salt may even be required to produce a favorable micelle concentration within the cleaning suspension. Most of the syndets are less sensitive to acids or moderately low pH conditions than soaps. Neither soaps nor anionic syndets are compatible with cationic syndets.

There are a number of different classes of chemical compounds that have been studied and patented for detergent usage. For simplicity, we will try grouping them into three categories.

1. The fatty alcohol and alkyl sulfates and sulfonate esters (F.A.S.)
2. The alkyl-aryl sulfonate esters
3. All other anionics

Groups (1) and (2) comprise most of the syndets marketed in the U.S.A. today for textile cleaning.

Of these three rough groupings, class (1) behave most like the true soaps as far as cleaning effectiveness is concerned. The fatty alcohol sulfates are produced from natural fats, such as coconut oil, in which lauric acid \( \text{C}_{11}\text{H}_{23}\text{COOH} \) is reduced to lauric alcohol \( \text{C}_{11}\text{H}_{23}\text{CH}_2\text{OH} \), which in turn is treated with sulfuric acid and neutralized to produce
C_{11}H_{23}CH_2--OSO_3Na, or sodium lauryl sulfate. The hydrophilic portion in this molecule, ____SO_3Na, is much stronger and more active than the ____COONa of the corresponding lauryl soap. Thus, this particular syndet turns out to be soluble in cooler water than the soap and is preferred by professionals for wool cleaning. Other similar sulfates are by-products of petroleum cracking.

The sulfonates which are also by-products of petroleum cracking have a very similar hydrophilic radical, ____SO_3Na, but in this case we might expect a little less activity towards water than from the sulfates. This class cleans much like soaps but is more soluble and less affected by acids, salts and hard water. The members of the class also work better at lower pH levels than soaps. We would expect them to be biodegradable.

The alkyl-aryl sulfonates (A__A__S), sometimes known as the alkyl-benzene sulfonates (A__B__S) are perhaps the most widely used chemical class of anionic syndets. Their main chemical characteristic is that the structural formula, in addition to a straight alkyl chain, contains an aryl or benzene ring to which a sulfonic acid radical is attached. Upon neutralization, with one of the solubilizing metallic ions, the aryl sulfonate metal complex becomes strongly hydrophilic. A typical formula for one of these is CH_3(CH_2)_xC_6H_4SO_3Na.

These detergents are synthesized mainly from by-products of petroleum cracking and refining. In general, they are more readily soluble than the F.A.S. types. For heavy duty cleaning, they require salts such as sodium sulfate or other thickeners to be added to build up a favorable micelle concentration. They are affected adversely by hard water, forming ions such as calcium, magnesium or iron. This is not so visibly apparent as in the case of soaps. They are less sensitive to sea water, and to acids, than either soaps or F.A.S. types, and can be used at lower temperatures. Some members of this class are rated as non-biodegradable and it is possible that their present widespread use may be restricted unless procedures to remove them from spent wash waters are devised.

The third general anionic class comprises the enormous group of syndets of other chemical families. Most of these have been developed for special cleaning purposes.

Alkyl-aryl sodium phosphates are highly regarded as detergents for use in drycleaning media. Others, some of which contain nitrogen atoms in the chain, have unique properties advantageous for cosmetic use or hair care.
Non-ionic Detergents

The non-ionic detergents bear no distinctive electrical charges, and a molecule is represented by a simple diagram: \[ \text{O} \text{ or } \text{O}^0 \] because in an electrolytic cell there is no deposit on either the cathode or the anode.

This main group of detergents is employed where an excess of stable foam or lather would be a nuisance, e.g. in home-type washing machines and mechanical dishwashers. As a rule, the non-ions are excellent solubilizers and give good results on soaking jobs where mechanical action is inadvisable. They are not affected by acids, alkalies, or salts in concentrations customarily employed in cleaning, and may be used in hard water. As a rule, they are quite soluble, although some, which are primarily lubricants, may be sparingly so. In order to form usable micelles for heavy duty cleaning, a thickener such as sodium carboxy-methyl cellulose (C.M.C) must be added. For soaking jobs, they must be used at the right temperatures. They are useful stain and grease removers, but may bleed dyes.

The non-ionic surfactants can be used in the same bath with anionics. There are three principal chemical classes of the non-ionic detergents:
1. The saponins
2. The ethylene oxide condensation types
3. The amine condensates

The saponins, although not widely used commercially, have found favor with textile conservation workers, perhaps for the generally admirable qualities of the non-ionics listed above. They are natural, detersive substances obtained from the barks of certain trees, as well as from nuts and fruits of a few plants. Some of the saponins are poisonous, but detoxified extracts are rated as excellent cleaners. They are expensive. The chemical formulae are more complicated than the classic soap chain and how the molecules do their work is not easily explained.

The ethylene oxide condensation non-ionics are probably equal in detergents properties to the saponins, far cheaper and more easily obtained. There are two chemical types as illustrated by the following diagrams:
1. \[ \text{O} \text{ or } \text{O}^0 \text{, an alkyl ethylene oxide where } \text{ indicates an alkyl chain and } \text{ an ethylene oxide chain;} \]
2. \[ \text{O} \text{, an alkyl-aryl ethylene oxide. In this case } \text{ indicates an alkyl-aryl group and the } \text{ denotes an ethylene oxide} \]
chain. Type (1) is apt to be grease solubilizers, or perhaps, in longer chains, semi-soluble textile lubricants. Moderately long molecules of type (2) configuration have been suggested as drycleaning detergents. Others may be good dye solubilizers.

The amine condensates differ from types (1) and (2) above, essentially in the fact that a nitrogen atom is introduced into the alkyl chain or into the aryl group, along with several ethylene oxide condensation units. Properties are similar to the above class.

Cationic Detergents

Cationic detergents are the third major group of surface active substances and the customary schematic representation is \(+\)\(\text{--}\)\(0^\text{-}\). Note the strong positive charge on the hydrophobic end. They are not compatible with the anionic detergents, and often form precipitates with that type. This is not true of the non-ionics which are sometimes used with them as synergists. The cationics are not considered as good general cleaners but do find use in special cases such as removal of bacteriological slimes and in disinfection work. At such times, when used for cleaning, a pH on the acid side increases detergent action.

Cationic detergents will exhaust out on fabrics and other surfaces, whereas the other detergent types may not. This can be noticed by a definite reduction in concentration in a solution to which a fabric has been exposed and extracted. This exhaustion factor is important in considering some of the special uses for cationics. One of these is an antistatic agent for nylon and woolen carpetings, or sheets of plastic film, or glass plates which tend to stick together when in contact. Surfaces so treated are easily separated afterwards.

Cationic detergents are used as fabric softeners. When cleaning an old fringed shawl or scarf, hours of laborious combing of the tassels after cleaning and drying may be saved by rewetting the fringe with a cationic solution and drying, before the job combing is attempted. Tangled fringes usually fluff out upon shaking afterwards.

A great many cationic type chemical compounds have been developed and patented in recent years. Many of these are for highly specialized uses as indicated briefly above. They may be roughly grouped into three main classes:

1. Long chain or fatty amines
2. Quaternary ammonium salts
3. Basic sulfonium and antimonium compounds

The first two named are, at present, the most common. The fatty or long chain amines are apt to be principally lubricants, softeners, and antistatic producers, and the quaternary ammonium salts are likely to be disinfecting agents and deodorizing sprays. Little has been published about the use of the third type. 13

Preparation for Cleaning

This step is not undertaken until all information regarding composition and condition of the specimen has been collected and evaluated. If the object is very weak and fragile, it may have to be protected and supported so as to immobilize it, without breaking it or causing undue loss of fibers. This may be done by placing it carefully, smoothly, on a stretched piece of synthetic fiber gauze (i.e., nylon or saran), and fastening it down by sewing, pinning, or adhesion. In some cases it will be necessary to use a very fine silk netting or crepelene next to the sample, both over and under. Depending on the amount of handling expected, the sample may also be covered with another piece of synthetic gauze. If the specimen happens to be a garment, it may be protected with a fine net bag of nylon or cotton. Fabrics made of synthetic fibers are preferred for protective layers; they do not shrink in water except under unusual temperature conditions. When it has been decided to clean the article in a washing machine, the two outer layers may be of aluminum or galvinized iron wire gauze. This preparation is time-consuming and tedious, but should not be neglected. Of course, with strong fabrics of good construction, these precautions may not be necessary.

Occasionally, in a composite specimen where fugitive colors, a special finish, or other problems might prevent cleaning in a particular medium, a resist protective treatment may be applied to prevent penetration of the solvent. For example, a starchy type chintz glaze should not be exposed to water. It may be protected by applying molten paraffin to guard during the wet phase. After drying the paraffin may be removed by drycleaning. Protection for a painted area during drycleaning is supplied by a coating of gelatin carefully applied. This might be removed by

digestion, if necessary, after drycleaning. Other preparation steps include removal of linings, buttons, and trim of various types, where possible.

Selection of Cleansing Medium

Choice of the cleansing medium will depend on the simple performance tests for dye bleeding and soil removal. The latter is made by rubbing a small test area with a white cloth moistened with water, followed by one moistened with detergent solution. Where dye bleeding is noted or where no soil pick-up can be seen on the white cloths, a test for effect of drycleaning solvents is made in the same way on a new area. It is important that all component yarns, colors, applique work, embroidery, painted or printed figures be tested. Where the specimen is extremely fragile, the tests may be made by using cotton tipped wooden medical applicators dipped in the various text mixtures. If necessary, the conservator may have to improvise other tests in miniature to arrive at a decision.

As a general rule, fugitive dyes behave better in dry solvents. Very old, fragile textiles are less affected chemically by dry solvents, and the fabrics are less apt to shrink. On the other hand, wet cleaning, properly managed, does a better cleansing job in most cases and is easier to control. Although solubilization soaking can be done in both mediums, water soaking is able to remove more soils and stains. Bleaching is not feasible in dry solvents, nor should digestion, sequestration, acid or alkaline reactions be employed.

Choice of Cleaning Technique

Mechanical handling is beneficial in almost every case of cleaning. After wetting the specimen, it is necessary to help the wetting and spreading action by submerging the specimen, or bringing fresh solution into it. Temperature control and judicious choice of surfactants are helpful. Time of contact or opportunity of contact is also important.

In each individual case, the extent of mechanical action will depend on the physical condition of the fabric. This is judged partly by the age and general appearance of the specimen and partly by the miniature cleaning tests described above. An experienced worker can soon tell (by rubbing a small area gently with a dry cloth, and again with cloths moistened with the cleansing media), whether it will withstand mechanical treatments as desired. Tests for more drastic action may be made by brushing, flexing or squeezing as desired.
Soaking

For very fragile pieces and fragments of textiles, soaking techniques with the specimen immobilized as described earlier, so as to prevent further disintegration, are suggested. There are five important aids to this technique. First, one must select a solubilizing agent which will act on the stain or soil. For example, if the soil is slightly acidic, a mild alkaline detergent may be indicated by the preliminary tests. Secondly, the soaking bath should be at the right concentration. This will range from about 1000 to 2000 parts per million, 0.1 - 0.2%. The detergent chosen should be one of predominantly solubilizing characteristics such as a non-ionic or an easily dissolved anionic type. (The patented or trademarked mixture should be about 40% alkali to 60% detergent, diluted to the concentration recommended above.)

Thirdly, the temperature of the bath is of great importance. For wet soaking, this may be maintained at about 37.5°C (110°F). This temperature is high enough to help the detergent molecules bombard the soil or dye particles vigorously, but not so elevated as to promote rapid chemical degradation of weakened fibers.

Fourthly, provision for circulation of the bath is necessary, to bring fresh solution in contact with and remove spent liquor from the fabric. This may be done by stirring or by moving the immobilized sample gently through the bath. Finally, since the exchange is quite slow, enough time must be provided for the penetration and solubilization to take place. Frequently, this time must be extended by refilling the bath with fresh solution. When this is done depends on observations of samples of the solution of color, turbidity, and other signs of soil removal activity, taken from time to time.

Soaking out techniques in drycleaning fluids are sometimes worthwhile. This is true especially where wet cleaning would cause dye bleeding or where it would engender fiber disintegration. In these cases, drycleaning solvent is mixed with about 3/4-1% of a drycleaning soap containing a very small amount of water. The temperature is maintained at 20-25°C (68-77°F). Circulation and mixing in the bath is important and the job may take a longer time than wet cleaning. Oxidation or other degradation factors are minimized, however, and the danger of damage is much less than in a wet-cleaning bath.

Sponging

Sponging techniques are important so far as minimizing the damage potential to the textile during cleaning. The fabric is spread out flat on
a surface and the cleansing medium is forced into it by sponge pressure to create a flow through and back. This system has a great many of the advantages of simple soaking but is much faster and cleaning is more complete. Obviously, the possibility of damage increases with heavy pressures and transverse rubbing. Slightly higher detergent concentrations are more effective in this case (0.18-0.25%) and temperatures of 27-32°C (80-90°F) are usual, since at this point, emulsification is desireable. Drycleaning by sponge action would be more practical and less likely to cause pile crushing on velvets or other pile goods, and, if carefully, done, on satins.

**Brushing**

Occasionally, an encrustation or massive soil deposit resists wetting and penetration by mere soaking or sponge pumping, and must be broken up by scraping or brush action. Where the fabric construction is reasonably rugged and fiber oxidation not advanced, brushing is a rapid way to remove soil. It is an especially good technique where overwetting is to be avoided. There is less danger of damaging the fibers when soft bristles are used. When transverse motion is necessary, the bristles should be slanted away from the direction or motion. Sometimes an obstinate crust will disintegrate by gentle tamping or stippling with the bristles vertical. This, of course, would not be a good way to treat a satin or a velvet, but heavy pile goods such as rugs, especially if relatively new, will withstand brushing very well. Brushing with approved drycleaning solvents is considered safer than with wet cleaners.

Occasionally, a deposit of dried paint or adhesive becomes so thoroughly set that it can only be removed by scraping with a blade-like instrument. A bone or wooden scraper may be purchased for this work. Metal instruments such as knives should not be used due to potential danger of cutting the fiber and staining from chemical action.

**Tumbling and Jetaction**

Modern washing machines are based on jetaction in some form. In the conventional horizontal tumbler, which reverses direction every 12-20 revolutions, the jet principle is subordinate to flexing. These machines are less damaging than they appear, and the danger of damage occurring is much less if they are lightly loaded, and operated with a relatively large volume of the cleansing medium at a slow speed. If garments or large specimens are prepared carefully by securing them between two layers of
metal cloth, and rolled into a cylindrical coil to fit into the machine, excellent cleaning can be accomplished with a minimum of harm. This is especially true of drycleaning.

Unfortunately, this type of equipment is being replaced by machinery which is smaller, crowded, and operates very rapidly. This machinery is unsuited for museum textile cleaning. Likewise, the usual home laundry machine, which operate on a reversing jet effect by changing the rotation direction of fins on a spindle rapidly, is not considered suitable and would probably tear up a fragile textile quickly, even if it were protected.

**Resoiling**

Redeposition of soil may be brought about by continuing the washing for too long in either wet or dry processing. It is most likely to occur when the temperature or pH condition within the water changes, especially in cooling. In drycleaning, a build-up of static electricity within the solvent will cause redepositing of soils. Whenever soil is redeposited, the fabric appears dingy and subsequent removal of soil is much more difficult. Resoiling may be avoided by changing the cleaning bath before suspended soil can settle.

**Rinsing**

Rinsing is an important step. Sometimes as many as five complete changes are necessary to get rid of soaps and some alkalies. Synthetic detergents, because of their greater solubility at lower temperatures, may require fewer changes. It is usually a good plan to reduce the temperature gradually through the several rinsing changes. This is especially necessary when working with woolen goods where sudden changes in temperature may contribute to excessive shrinkage.

In cases of dye bleeding, especially in woolen or silk materials, the final rinse is usually acidified up to about 1 or 2% concentration of a milk acid, such as acetic, or an acid salt, such as zinc or ammonium silicofluoride. The pH should be about pH 3 to pH 4. This is called **scouring** and is also beneficial because it neutralizes adsorbed alkalies on cellulosic fibers which have been accused of catalysing brown stain development as the fabric ages.

Some dyes used for cottons or linens require salt brine as a setting agent. In this case, the concentration of salt may be as high as 5% in order to prevent bleeding.
Extraction

After rinsing, the immediate removal of excess moisture is very important. If the fabric remains saturated, dyebleeding or transfer is still a serious threat. Quick extraction by any means that the fabric will withstand, will minimize this dye staining and will help to speed up the drying process.

Extraction methods vary according to the size of the specimen and individual estimates as to how well it will withstand the physical stresses and strains. Perhaps the simplest method is drip drying with the fabric suspended. In this case, the excess liquid drains to the bottom and the lower edge is usually stained. If the specimen is not very large, this may be overcome by spreading it out horizontally on a screen or net. If the fabric is very weak, it may not withstand hanging.

A second simple method is by blotting absorption. For this, the article is laid out on a flat surface between layers of absorbent materials such as cotton cloths, paper towels, or felts. Flat weights are placed on top to provide contact pressure. If this is done quickly and the absorbent materials frequently replaced by dry blotters, this technique gives satisfactory extraction with the least dye transfer or structural damage. In those cases where protective gauze or layers of permeable temporary reinforcements are necessary, the excess fluid removal is not hindered appreciably.

Wringing or twisting or torsion, although probably safe for strong fabrics, produces shrinkage and is apt to cause wet dye transfer stains. It is not recommended for fragile or worn specimens.

Squeezing between rubber covered rollers is a rapid way of removing excess fluid from flat goods. If the fabric is not wrinkled when feeding it between the rollers, and the pressure is adjusted according to the particular condition of the materials, very little structural damage is likely. It is not a good way of handling garments, however, because of possible crease setting.

Extraction by centrifuge is probably the most widely used method in professional cleaning and in home washing machines. It is suitable for garments and small articles and, if operated intelligently, will remove as much or more moisture than squeeze rollers, but not as rapidly if time is compared by the piece. It is not so good for large flat work because the whirling basket must be loaded so that weight is distributed equally around the circumference. If the work is not arranged carefully in a smooth neat
coil, wrinkling and crushing is likely to occur and occasional contact dye bleeding is possible. Excessive compacting and wrinkling may be avoided by placing garments in net bags before loading in the machine. If the garments are very old and fragile they may be rolled between two pieces of wire gauze before coiling around the inside of the centrifuge basket. Medium-sized household articles such as bed spreads, table linen and rugs, if not too large, may be treated in the same way. After bringing the machine up to top speed, the power should be cut off and the machine allowed to come to a stop. Whether the load is spun for a longer time depends on the size and rotating speed of the machine, also the apparent physical condition of the load.

Centrifuging or the blotting method of extraction is preferred in drycleaning. For fairly strong unlined rugs and tapestries, squeeze rolling is a preferred way of extracting excess water. The solvent in drycleaning will damage the rollers and in this case, extraction or blotting is safer. Linings must be removed or loosened because unequal shrinkage is the cause of much creasing and damage in extraction.

Drying

In wetcleaning, speedy drying after extraction is very important. The reason for this is that fibers that are just damp and exposed to the air, oxidize rapidly. In cellulose fibers, a brown colored intermediate substance, resembling an acid, is formed at the line of drying. If the residual moisture is not evaporated in place, it will travel out by capillary action to a line or border where evaporation and the supply of water are in equilibrium, and at this point the stain concentrates and becomes more easily recognized. If the line happens to be at the end of a pile or a yarn surface, it may result in an overall stained spot. If it is a candlewick tufted construction, a heavy brown line will result. The color can be removed from cotton or other cellulosic products by wetcleaning or mild bleaching unless it has been mordanted accidentally. If, however, the stain has contacted wool, a fast dyeing occurs and it will not wash out. Drastic bleaching is about the only remedy.

This staining does not happen in drycleaning except where the cleansing medium contains a heavily moisturized soap-solvent, and even, then, it would probably be on a sugar spot where a color difference could not be detected before cleaning was started.

The best natural dyeing of textiles occurs when they are exposed to
a warm dry wind on a sunny day. This illustrates the three main requirements for good drying, which are:

1. Heat to evaporate the moisture or solvent
2. Dry or low humidity air, which will accept the moisture or solvent quickly
3. Rapidly moving air to overcome stagnant surface film resistance to heat transfer and moisture acceptance by the air

Although heat may be applied to a textile by radiation or by conduction from contact with a hot surface, the safest way is by forced convection with air as the carrier of heat. When air is heated, its relative humidity is lowered and its moisture acceptance ability is increased. In addition, it can give up more heat to the wet material. If this air is forced through or past the textile surface rapidly, the evaporation rate is greater than if the fibers are surrounded by a stagnant air film. Nevertheless, there are certain limits to the air temperature, velocity and humidity that should not be exceeded in drying many fragile or aged fabrics.

As long as the fiber surfaces are wet, the air temperature may be maintained at a high safe point of about 60°C (140°F) because if the air before heating is assumed to be at 20°C (68°F) the evaporating water and the fiber surface will be much cooler than the drying air. This final surface temperature will depend on the air speed and how fast the cleansing liquid passes from the interior of the fiber out to the surface. When the fiber surface becomes dry, its temperature will rise to that of the air stream and at that time cellulosic dehydration products tend to form more intensely colored substances. As the temperature increases above this assumed safety level, the dehydration effect becomes even more noticeable. This can be avoided by lowering the temperature of the drying air as soon as the surfaces appear dry. During the final stages of the drying period, the air temperature and relative humidity should be the same as that of the room where the textile is to be stored.

From empirical tests and calculations made a number of years ago, it was concluded that a reasonable air speed for drying suspended rugs was about 400 ft/min (about 110 m/min). This correspondsto a gentle breeze of about 4 1/2 mi/hr and was not likely to cause whipping or snapping damage. If the textile was flat and protected by a supporting gauze, this air velocity could be increased considerably, perhaps to four or five times the
speed of a hair dryer.

Textile conservationists may find it necessary to set up special drying facilities for very fragile problems. Drying equipment will vary in each case, but basically will consist of portable electric fans and electric or steam heated radiators. As long as the textile surface is wet, damage is small even though radiant heat is directed on the fabric. This heat must be cut down as soon as surface drying is apparent.

Commercial cleaning establishments have developed several different types of mechanical dryers, such as drying tumblers, drying cabinets and lofts, curtain stretchers and dryers, wind whips and combination drying and pressing machines. Whether any of these would be suitable for a particular job would depend on the strength and ruggedness of the individual specimen.

Drying tumblers are perforated metal cylinders that revolve inside a metal enclosure through which heated air is passed. They are commonly used in both wet and drycleaning plants and home laundry installations. These machines are satisfactory for drying garments and individual small textiles, especially if they are relatively new and strong. They may also take delicate goods where the individual pieces are secured in protective net bags or packages. Because there is much flexing and dropping, and the time in the machine is half an hour or more, these dryers may not be suitable for old and much worn specimens.

Drying cabinets or rooms are enclosed spaces where the articles may be hung or draped over poles or on hangers and heated air circulated between the pieces. Temperatures range below 60°C (140°F) for wetcleaning, or about 32°C (90°F) or 49°C (120°F) for drycleaning (depending on whether Stoddard solvent or 140°F flash solvent is used in the cleaning process). According to the space available, they are suitable for drying garments on hangers, rugs, tapestries, and other moderate- to large-sized pieces. Rate of drying depends on the temperature of the air, its relative humidity, the effectiveness of the circulation within the space, and the air supply. Usually drying is much slower in this kind of equipment than in drying tumblers, but there is much less likelihood of damage or wear.

A wind whip is a machine for drying wetcleaned garments. The garment is buttoned and clamped, or pinned over a form and suspended from a hanger. Heated air from inside the form is forced through the fabric. Drying is very rapid and when draping and suspension is done with care, there is very
little possibility of wear or damage. Staining, either from oxidation or from dye bleeding, is minimized because the evaporation rate is faster when the air passes through the fabric than when it travels parallel to the surface. There is also less opportunity for the moisture to move laterally by capillary action.

A similar drying system for textile fragments may be improvised from a box, the top of which is covered with air permeable cloth or screen, with a bottom fitted to an electric vacuum cleaner nozzle. By blanking off those parts of the screen not covered by the fragment, a positive air flow through the fabric can be assured when the vacuum is operated. A moisture trap between the vacuum cleaner and the box may be necessary if the fragment has not been extracted completely. This improvisation must not be used for drycleaning work because of fire, explosion or toxic gas hazards. Heavy duty professional vacuum cleaners can be purchased, however, and these are considered safe for this work.

Household flat work and linens are usually dried commercially by passing them over heated rolls. This system irons them at the same time. Curtains, especially after starching, are stretched to size and dried by radiant heaters. This type of drying is not recommended for most museum textiles.

Finishing

The last step in fabric manufacturing is finishing. It is also the last thing done in cleaning, and is necessary so as to present the completed job in a smooth or otherwise attractive condition. The basic reason for this is that with natural fibers under the usual processing and manufacturing techniques used for producing most historic textiles, precise uniformity of fibers and of the scouring, dyeing, spinning and weaving is not possible. This in turn, results in variations of moisture, dye and other chemical substance, causing differences in wrinkling, shrinkage, lustre, flexibility and feel in two similar textiles or even in parts of the same piece. For this reason, it is the usual practice to try to even out the overall appearance with after-treatments or finishing.

In finishing processes, there are three main things to be done. First, the fabric must be plasticized; secondly, it should be dimensionally restored and smoothed out; and thirdly, it may be necessary to stabilize it in that condition.

By plasticizing, we mean restoration of the textile to its customary
smoothness and appearance. This is nearly always necessary, especially if the fabric has been dried by heat and air, because it will have been over-dried. This is true in drycleaning as well as wetcleaning.

If the fabric is over-dried the material will be harsh, wrinkled and, if it is old, it may be brittle. All these are fundamentally due to lack of proper moisture content in the fibers, sometimes known as regain. At any temperature, there is a corresponding moisture content for every relative humidity condition of the air in contact. The moisture content increases as the humidity increases, but not in direct proportion. The shape of the curve of moisture content against humidity differs for each fiber. Unfortunately, after over-drying, the textile does not recover quickly unless moisture is forced into the fabric, the yarns and the individual fibers.

The best quick ways of moistening the fibers are by dampening the fabric with water and by steaming. Water applied by spraying requires an appreciable time for penetration and is not uniform. Steaming, if properly done, is far more satisfactory if suitable equipment is available. A suggestion is that an electric steam iron, set to produce steam, is held just above the fabric but not in direct contact. The material should be laid out flat on a padded surface such as an ironing board. When the area under the iron appears to be conditioned, a mitt made of a cloth pad is pressed on the area to smooth out wrinkles. The iron is not permitted to come in contact with the specimen unless the fabric is strong and can withstand ironing. By alternating steaming and pressing with a pad, the whole area of the specimen can be covered. If more sophisticated steam pressing equipment is available, larger areas can be smoothed and time saved. For napped goods, a soft brush or whisk broom may be drawn lightly over the steamed area to produce a pleasing effect and avoid flattening.

In some cases, a good surface appearance may require fixing or starching. When this is necessary, the specimen must be wetted with the fixing agent before it is shaped and ironed. The type of fixing agent or starch has been broken down by cooking, or has been treated to make it cold water soluble, it may become yellowed or turn brown after aging for a while. Potato and corn starch are more inclined to do this. Wheat and rice starch are finer grained, more easily dissolved, and less likely to be degraded towards colored substances. Ironing temperatures should be as low as possible because the starch is easily toasted and degraded to a point where
the color will show.

Instead of starch; gelatin, gum arabic, gum tragacanth, and flaxseed are used, on occasion, to provide special degrees of stiffness, luster, and handle to the finished textile.  

CHAPTER III

CONSERVATION METHODS

The conservation of textiles can be attained:
1. By taking measures which eliminate or reduce the harmful effects of outside factors such as light, too high of relative humidities, polluted air, etc.
2. By treatments which are carried out with or on the textile objects
   The latter can be divided into three groups:
   (a) Application of needle techniques
   (b) Application of natural and synthetic adhesives
   (c) Combinations of (a) and (b)

   The Application of Needle Techniques
   For the conservation of textiles by thread and needle mending different methods can be followed. The decision as to which one to choose should be made according to the form, condition and the historical and aesthetic value of the object.

   Form
   The treatment of a flat textile (or textile fragment) will generally be different from the treatment of a dress. With flat textiles, supporting fabrics can be used when the loss of suppleness is not too great. In the case of a dress made of a supple material, however, the application of even a very thin material will greatly harm the drape. Ecclesiastical garments are rather stiff and can be spread out flat, so, in this case, the methods for flat textiles can be generally applied.

   Condition
   The line between 'good' or 'bad' conditions in specimens is obviously not clearly defined; it depends on the subjective impressions of the person judging. A more objective view is to say that whether a textile is judged to be in a good or bad state depends on what is to be done with the conserved object. It may be in a perfectly good state to be kept either lying in a drawer, or fixed between glass plates, but not suitable at all
to be exposed, hanging, in a representative room.

In general, an object is considered to be in good condition if this condition does not vary widely from the original, i.e. the object can be fairly well handled and does not show too many spots. When this is the case, it will suffice only to fasten the frayed edges and the loose threads around the holes with a fine, regular stitch. If the structure of the textile allows it, and a hole is not too large, then darning the object can be considered, according to fabric weave. If this is not possible, a piece of fabric, similar in structure and color can be sewn behind.

If the textile is in poor condition, a supporting base must be considered. This may only mean that it is put on a stiff base, e.g. a linen-clad wooden plate and covered with a glass plate. In many cases fixing it on a flexible supporting layer will be preferred. This can be done either by fastening it at the edges with fine flat stitches or buttonhole stitches, or by fastening very weak, badly worn spots following the 'laid and couching' technique. Where there are loose threads, these become the 'laid' thread and the thread chosen for repair is the 'couching' thread. This technique can be applied, for example, in repairing gold brocade.

If it is necessary to fasten pieces of fabric which are in danger of coming loose, threads can be laid across and fixed with stitches made with the same thread as they are laid (self-couching). It is also possible to first lay some threads at smaller or greater distances on the fabric and then to fasten them with another thread, the couching thread (couching proper).

Figure 14 - Self-couching

Figure 15 - 'Couching proper: (a) laid thread, (b) couching thread
Figure 16. Tacking over the full length as well as over the full breadth will cause rumpling along the rows of tacking stitches.

Figure 17. (a) Auxiliary threads to be removed after tacking; (b) alternate rows of tacking stitches (14-20 cm in length) only over the length of the fabric.

Figure 18. Alternate rows of tacking stitches over the length as well as over the breadth of the fabric.

In some cases one may want to affix a fabric not only at the face, but also at the back. The fastening of the three layers (two layers of supporting fabric, with the object in between) can be done with tacking stitches. They should not be applied over great lengths, e.g., across the full length or the full breadth, because in that case the layers will not remain in position and rumpling will occur along the rows of tacking. Alternate rows of tacking, 140-200 mm in length, seems to yield the best results. The preceding stitches might be incorporated for fastening threads and fabrics. When embroidery is to be repaired, the choice of technique will naturally be decided by the stitch used in the object. It is then necessary, in some way, to give visible indications of what spots are repaired, as has been stated in the introduction.

Because any conservation should also be aesthetically justified, the conservator should be master of all needle techniques, and should also have the artistic feeling to maintain the balance of the work of art. The correct thickness of a needle and the right yarn (material, color, number) should be chosen for each object repaired. Thus, silk fabrics must not be repaired with mercerized cotton yarns; first, because the difference in material will remain visible however beautiful the gloss of the yarn may be; secondly, because the yarn will always be too thick, even after splitting; and thirdly, because the simple thread obtained by splitting twined yarn is too hairy, a disadvantage which may be partly removed by paraffinizing. Silk yarns are best to use. The great length of the fibers makes them easier to split. These yarns are becoming more and more difficult to get, and synthetic filament yarns (nylon, polyester) may have to be used instead.

Sometimes it is feared that split silk or synthetic filament yarns may be too weak for this work. It has been found, however, that in museum objects the forces per stitch are so small that very thin yarns can be applied without any risk. In any case, it is thought by some people that yarns used for repair should wear sooner than the fabric. This proposition is derived from the clothing industry which uses yarns that, in case of forces exercised at the seams, will break ahead of the threads of the fabric, thus avoiding irreparable holes. With museum objects, this problem generally plays no part, except when costumes and uniforms are worn for shows. Fairly great forces might be exercised when textiles are fastened on a supporting fabric under considerable tension. In this case it is desirable that the
tacking threads should break. When the yarn is thin enough, the conservation work is almost invisible. Moreover, no holes are made in the object, as is the case with thick yarns.

Value of the Object

The time factor, which also involves cost, often plays a great part in the choice of needle technique. Working with thin yarns, with regard for aesthetics, takes considerably more time than working with thicker yarns, and consequently raises the cost of the conservation work. The historical and aesthetic value of the object must determine when such great expense is justifiable.

In general, serious objections must be raised to proceeding with a less aesthetic method of conservation owing to limited funds. In this situation, it is better to simply clean the object and to store it under the right surrounding conditions.

Supporting Fabrics

The supporting fabrics to be applied should be chosen to correspond with the object. A first requirement is that they should be as transparent as possible, so that the object can be clearly studied from face and back, e.g. in order to analyze the structure of the fabric. This requirement can only be partly complied with, for no matter how transparent a fabric may be, it will always veil the structure and the colors to some degree.

Most transparent fabrics on the market are also too stiff for this purpose, having been treated with stiffening agents. There are, however, some factories which still deliver thin fabrics to special order. (Note: Owing to great changes in the various branches of the textile industry it cannot be certain that the fabric available at present will also be obtainable in the future.)

A note of warning is sounded here against coarse canvas fabrics, as used for cushion slips, or thick tulle fabrics. Their texture becomes imprinted into the thinner material of the objects to be conserved. Moreover, there is the risk that the hardness of their yarns will cause further wear of the conserved object when it is handled.

Conservation Methods Using Only Natural and Synthetic Adhesives

Natural Adhesives

The methods of this category may not have been applied as long as methods using needle and thread, but they have been in use much longer than
is usually supposed. At the end of the last century, and in the beginning of this century, many flags and banners were preserved by glueing them on or between textiles by means of a kind of starch paste, e.g. rye-flour and wheat-flour, gum arabic or some animal glue.

In many cases the results of this gluing were anything but satisfactory. Often, the adhesives were deteriorated by mold and bacteria, when the textiles were exposed to humid surroundings, or wetted by leaking (filtering) water and condensation. Additionally, in the course of time the glue between the old and new material became very brittle and/or hard; the flexibility of the textile was diminished greatly. This was a great disadvantage, especially for those objects where suppleness was an important feature.

Often smaller fragments of fabrics, such as samples or small pieces of Coptic and Peruvian textiles, etc. were stuck on cardboard by means of some natural glue. In these circumstances perhaps the decrease in flexibility was not so important; but a much more serious disadvantage was that the glue often became visible at the front as dark spots.

Although this way of conservation can be severely criticized, it must be realized that the greater part of these objects would have been lost, if they had not been preserved in this manner. Today the application of glued of vegetable or animal origin for the conservation of ancient textiles has almost completely been abandoned. In Russia, however, particularly in the Hermitage Museum in Lenengrad, they still preserve textiles by sticking them on a textile support with wheat-flour paste.

Several recipes have been developed because of the different textures and thicknesses of the fabrics which have to be treated. The different compounds in the recipes have a specific function. Wheat-flour is the glue. Gelatine serves to improve the properties of the glue by increasing the sticking power and making the adhesive film more transparent. Glycerine has the property of binding water, so that the glue never dries up completely. It will always contain some percentage of water and keep a certain suppleness and elasticity even when the surrounding atmosphere has a low relative humidity. Alcohol has a double function: first it reduces the viscosity to some extent, and secondly, as it is more volatile than water, it accelerates the first phase of the drying process. Benzoic acid and thymol are pesticides, which prevent the development of molds and bacteria.
**Table 5 - Three Recipes for Conservation Adhesives**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Recipe 1 low viscosity</th>
<th>Recipe 2 medium viscosity</th>
<th>Recipe 3 high viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>wheat-flour 30% (1st quality)</td>
<td>1-2</td>
<td>3-4</td>
<td>18-20</td>
</tr>
<tr>
<td>gelatine (pure)</td>
<td>0-25</td>
<td>0-25</td>
<td>0-25</td>
</tr>
<tr>
<td>glycerine (chemically pure)</td>
<td>2</td>
<td>3</td>
<td>3-4</td>
</tr>
<tr>
<td>ethyl alcohol (96%)</td>
<td>10-15</td>
<td>10-20</td>
<td>10-20</td>
</tr>
<tr>
<td>benzoic acid or thymol (chemically clear)</td>
<td>0.1-0.2</td>
<td>0.1-0.2</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>add distilled water to 100%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 6 - Additional Recipes for Conservation Adhesives**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Recipe 4</th>
<th>Recipe 5</th>
<th>Recipe 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>wheat-flour 30% (1st quality)</td>
<td>0.25-5</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>gelatine (pure)</td>
<td>-</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>glycerine (chemically pure)</td>
<td>2</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>ethyl alcohol (96%)</td>
<td>15-20</td>
<td>15-20</td>
<td>30</td>
</tr>
<tr>
<td>benzoic acid or thymol (chemically clear)</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>add distilled water to 100%</td>
<td>to be calculated</td>
<td>to be calculated</td>
<td>60</td>
</tr>
</tbody>
</table>


Recipe 1 has such a low viscosity that when the textile is impregnated by it, although after drying, there is hardly any perceptible influence on the appearance and the feel.

Recipe 2 has a distinctly higher viscosity than recipe 1, so that in general, no impregnation will take place, except with fabrics with very open textures.

In Recipe 3 impregnation is totally excluded. A close film of adhesive forms between the old textile and the supporting fabric, which creates a 'sandwich' structure. This paste is recommended for coarse, thick and heavy textiles, such as tapestries.

Whereas recipes 1, 2 and 3 are primarily applied to fix the textiles on a support, recipes 4 and 5 are meant as reinforcing agents. The fragile textiles are impregnated with them, and loss of fibers at the front will be avoided. Recipe 6 is in use for the improvement of the suppleness of stiff fabrics, also by impregnation.
About 20 years ago the development of conservation methods by means of synthetic resins started independently in various laboratories. In the beginning, more often than not, the results obtained were not at all satisfactory, for several reasons: the properties of synthetic resins available at that time could not satisfactorily meet the demands of a good conservation of textiles, there was not enough experience in a proper application of these products, and the main cause of the only very moderate success, was that the scientific researchers who worked on these methods were not sufficiently aware of the specific demands of this particular field of application. Owing to frequent contact made by these researchers with art historians, who are specialists in the field of museum textile objects, they are now better known. Moreover, in industry various types of synthetic materials are manufactured whose properties can now be used satisfactorily.

Properties of Synthetic Resins

To understand the properties of the synthetic resins and their behavior in the course of time, it is necessary to enter into a discussion on what resins are, and the main principles of their manufacture.

According to the definition from the 'Report on nomenclature in the field of macromolecules', J. Polym. Sci., 9, No. 3, 265 (1952), a resin is 'an amorphous substance or mixture, of intermediate or high molecular weight, which is insoluble in water but soluble in some organic solvents, and which at ordinary temperatures is either a very viscous liquid or a solid which softens gradually on heating. All solid resins are thus thermoplastics, and thermoplastics obeying the solubility criteria just mentioned are resins'.

The synthetic group may be divided further into two sub-classes: the thermoplastic and the thermosetting types. The thermoplastic adhesives can be melted and made to flow. Upon cooling, they resolidify or regel. On the other hand, the thermosetting types polymerize or set up more strongly as the temperature rises.

Cellulose esters, cellulose ethers (such as carboxymethyl cellulose), acrylic esters, polyamids (like Nylon), polystyrene (like transparent

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buttons), polyvinyl alcohols and others are examples of the thermoplastic group.

The thermosetting resins and adhesives are combinations of urea, melamine, phenol, resorcinol, furfural, epoxy and polyester substances.

Many of the adhesives in either division are unsuitable because they discolor with age and continue to harden beyond a satisfactory state.

Among the thermoplastic types, polystyrene and polyvinyl alcohol compounds promise the best results for museum work. This is because they are clear and can be used at relatively safe temperatures.

The thermosetting types can be solidified at relatively low, safe temperatures by the judicious employment of catalysts and redox reagents, pH and time conditions.

The surface that we may be working with and the final product that we hope to achieve have a great bearing on our choice of adhesive. If the surfaces are the same material, then we should use an adhesive that will dry or cure into the same hardness, as co-efficient of expansion and flexibility of the two substrates. If they are different materials, we must choose one that will adhere tenaciously to both surfaces, yet have sufficient internal mobility and flow to permit unequal expansion.

There are two ways of accomplishing this flexibility. First, we may mix an additive into the adhesive which will prevent complete drying. Sometimes these additives are merely internal lubricants. Second, we may arrest the chemical reaction before it goes to completion. On occasion, we may add substances to the mixture to interfere with the reaction. These are in a sense negative catalysts. Or we may keep the temperature down so that the reaction rate is very, very slow. Chemicals used to control stiffness are generally called plasticizers. Those for slowing down the reaction are called inhibitors.²

Thermoplastic resins are composed of large linear molecules (linear macromolecules), which are formed from small molecules (base units) by the process of polymerization. When in these macromolecules only one type of small molecule takes part, or different types in regular sequence, these polymers are called homopolymers. Where different types of small molecules

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in irregular sequence take part, they are called copolymers. Often a certain polymer can only be attained by a chemical transposition of another polymer. So polyvinyl butyral has to be prepared from polyvinyl acetate via polyvinyl alcohol. The procedure is as follows:

\[
\begin{align*}
\text{VINYL ACETATE} & \rightarrow \text{POLYVINYL ACETATE} \\
\text{POLYVINYL ALCOHOL} & \rightarrow \text{POLYVINYL BUTYRAL}
\end{align*}
\]

The saponification and acetalization reactions are obviously not 100% complete, so polyvinyl alcohol will always contain a number of acetate groups and polyvinyl butyral a number of acetate and hydroxyl groups.

The physical and chemical properties of the resins are dependent on:

1. Average degree of polymerization (average number of base units per molecule)
2. Distribution of the degree of polymerization
3. Presence of different groups as a result of incomplete transposition reactions
4. Pollution by chemicals such as initiators, inhibitors, reaction accelerators, etc., which were necessary for the polymerization process
5. Presence of plasticizers, chemicals which may have been added after the polymerization process (external plastification). In the long run a reduction of the flexibility and an increase of the brittleness of the resin film may appear, because these plasticizers are more or less volatile. It is also possible that they have been built into the molecule during the polymerization process, which is, in fact, a kind of copolymerization.
this case there is an internal plastification, and evaporation of the softening component will never take place.

Requirements for Conservation

Synthetic resins are only useful for conservation purposes when they have no noticeable influence on the appearance (visual and tangible), the colors, and the flexibility of the textiles. It is evident, however, that these requirements can never be met completely.

Another very important demand is that the resins are not subject to degradation under the influence of light and the surrounding atmosphere. This means that a film of the resin:

1. Has to keep its solubility in its solvent
2. Must not yellow
3. Must not give noxious compounds on decomposition
4. Must not show a decrease of sticking power
5. Must not have an ill effect on the aging of the textile material or on the fading of dyes
6. Must keep its flexibility

There have been plenty of experiments with plastics with regard to their usefulness in textile conservation, but only a few members of the family of polyvinyl compounds, as well as acrylates derived from them, meet the demands in an acceptable manner.

Polyvinyl acetate in the form of an aqueous dispersion is mainly used for gluing on a support. It is, however, less suited for impregnation, because even in low concentrations, it has a clearly noticeable effect on color, gloss and character of the fabric to be conserved. However, when it is necessary to impregnate a textile which is entirely or partly degraded to such a degree that a nearly continuous loss of fibers takes place, then this can be done with polyvinyl butyral. With low concentrations, 0.5% - 1.5% in ethyl alcohol, dependent on the thickness and the porosity of the fabric, no noticeable effect on color and gloss occurs, and there is only a light effect on the flexibility. Another agent for impregnation is soluble Nylon in a 1-5% solution in methyl alcohol which also gives very satisfactory results. Modocoll E. is also used as a successful agent.

Description of Conservation Methods with the Aid of Synthetic Resins

The application of synthetic resins can take place in three ways:

1. Adhesion on a supporting base and impregnating simultaneously
2. Impregnating the fabric without fixing on a base
3. Adhesion on a supporting base without simultaneous impregnation

1. This method, where adhesion on a support and impregnation take place simultaneously, often yields an insufficient result. The concentrations of the glue solution minimally required (5% or more) to guarantee good adhesion between the two layers are so high that the appearance is unfavorably influenced.

Among methods in this group is the Sieders method, in which flat textiles such as flags, banners and textile fragments are glued on to a stiff transparent base with the aid of 4-5% solution of polyvinyl alcohol in water. Glass or a sheet of polymethylmethacrylate (Plexiglas, Perspex) is used for a base. Polyvinyl alcohol, however, which in a fresh condition is soluble in water, has too low an adhesive power even in these concentrations. The objects easily become detached from the base, especially if the fabrics still contain tensions as a result of the weaving process, or unequal tensions as a result of locally occurring painted parts. Moreover, a flexible base is preferable to a stiff one, and for this the sticking power is far too low. Finally, it appears that polyvinyl alcohol becomes insoluble in water over the course of time, so that one of the attractive properties of this synthetic substance has been lost.

Another polyvinyl compound soluble in water, polyvinyl pyrrolidone, appears subject to change and, moreover, is an easy prey for fungi and bacteria in damp surroundings.

Polyvinyl butyral soluble in alcohol gives the most satisfaction, although even here in concentrations of 5% or more color, gloss, suppleness and touch are influenced disadvantageously.

From this it can be concluded that glueing and impregnating should never be done at the same time.

2. The polyvinyl compound, polyvinyl butyral, which appears to be most suitable for simultaneous adhesion and impregnation, is also best suited for impregnating textiles which have become so brittle and fragile that a reinforcement is necessary to prevent further loss, by breaking of textile fibers. The concentration should not be high (0.5 - 1.5% is suitable).

It is a well-known fact that in the case of wall hangings, very serious wear occurs where the combination of a woolen weft, dyed dark brown with the aid of iron containing dyes, and a silk warp are used. To prevent further deterioration the tapestries can be sprayed with a 1%
solution of polyvinyl butyral in ethyl alcohol. The applied quantity is sufficient for the adhesion of the fibers, but on the other hand so small that the colors, the appearance, and the touch will not change.

The treatment was adopted in the Netherlands in 1961 for wall hangings in a very bad state of repair. Up to now they appear to be safeguarded against further loss of fiber.

3. It is possible to glue a textile object to a base without it being impregnated at the same time. First the support is impregnated with the glue solution. After the glue has dried, this fabric is sprayed with the solvent used for the glue with a mist spray. By this means the adhesive layer in the supporting textile becomes sticky, and the old textile can be laid on the support, which results in the adhesion of the two textiles without the old material being impregnated. In actual practice this method is very difficult to carry out. Even if the glue layer is moistened only slightly too much, there is a great risk that the glue will become liquid to such a degree that it will ooze through the fabric, producing unsightly dark spots on the face. When too little solvent is used to moisten the glue layer, it does not become sticky enough and insufficient adhesion takes place. A great disadvantage is that it is necessary to execute the mounting of the old material quickly and directly in the right way, as displacement of the fragments on the base is impossible.

This lining method is theoretically attractive, but in practice it is very difficult to perform, owing to the complexity of execution and the resulting risks.

The method presently considered most suitable for adhesion on a base, is the so-called 'heat sealing' method. Polyvinyl acetate resin, which possesses a low melting range, about 70-120°C, is used. In the Netherlands, a mixture of two types of aqueous dispersions is used successfully, namely, Mowilith DM5 and Mowilith DM VI. After being spread out on a flat polyester foil, such as Melinex, the supporting fabric is impregnated with a mixture consisting of 1 part Mowilith DM5, 1 part Mowilith DM VI and 3-4 parts distilled water.

When drying of the polyvinyl acetate layer is complete, polyester foil is drawn off the impregnated base and the latter is spread out, glossy side up, on a new foil. Next, the old textile is spread out in the right position on this base in such a way that weft and warp of the two fabrics
lie parallel. Then, with the aid of a warm iron (temperature of about 80°C, because the polyvinyl acetate film becomes sticky at this temperature) the two textiles are joined together. It is necessary to put a piece of Melinex foil between the iron and the textile that is to be lined, so that on spots where the old textile shows holes the polyvinyl acetate film will not stick to the iron. The lined fabric is stripped off the Melinex foil only after it is perfectly cool.

With very thin, flexible fabrics the flexibility decreases too much when using this lining method. It is certainly advisable not to impregnate the base entirely with the polyvinyl acetate dispersion, but only locally, for example, using a square pattern or a dotted diagonal pattern. Consequently, there are less fixing points between the two textiles, flexibility increases, but the result from a viewpoint of conservation decreases. The same is true in the application of a needle technique for conservation of old textiles, because as the density of the stitches made becomes lower, the conservation quality becomes poorer.

It is evident that where the old textile is put on a supporting base without being impregnated simultaneously, the result is only partial conservation. The old fabric itself, and especially the front which catches the most light, is in no way safeguarded against further deterioration. It is often necessary to spray the front of the old textile with a solution (1-1.5%) of polyvinyl buryral (Mowital BH 10) in 96% ethyl alcohol after lining. In this case the liquid should always be sprayed on, because the polyvinyl acetate would be dissolved and would ooze through to the front of the fabric, if applied with a pencil.

Conservation Methods with Combined Use of Needle Techniques and Adhesives

When confronted with the problem of conserving an old textile, a choice of the conservation method will have to be made, according to the nature of the object and condition.

If several methods are possible, a sewing method should nearly always be preferred to an adhesive method, as sewing methods are more natural to a textile. Yet there are many cases where the use of sewing alone no longer allows a satisfactory conservation to be attained. If this situation exists, there is no need to decide immediately on a complete adhesive and/or impregnation technique, for often a combination of several methods can be the best solution to the problem. This is particularly true for those
textiles consisting of different materials, such as costumes, fans, parasols, shoes, uniforms, etc. There are also cases, especially where there is much local wear, where one section of the material is locally lined, and the rest sewn on to a supporting layer.

The function of the textile also should be considered in the choice of methods to be used. The decision to line a chair covering will be arrived at sooner than the decision to line a tapestry wallhanging, because the chair covering demands less flexibility but greater strength.

From the preceding it appears that good execution of conservation and restoration work on old textiles depends as much on a skillful choice of method as on the way in which the method is actually executed. It is, therefore, important that the conservator should possess a thorough knowledge of various textiles, a feeling for style and aesthetics, and most of all, wide experience in the field of textile conservation. When complete mastery of all available techniques has been attained, good results can be achieved. 3

Conservation Techniques for Archaeological Textiles

The particular techniques applied to the conservation of textiles depend not only on the raw material, but generally, on the nature of the specimen as well. Coarsely woven fabrics need different treatment than the very thin fabrics, and textiles of great age and historical importance must be treated with means unlike those utilized for specimens of purely decorative value.

Basic Principles of Conservation

1. The technique of conservation has to be maximally reversible, that the materials applied and/or the technical additions can be again separated from the original without causing any detrimental effects.
2. Where chemicals are applied, the quantity used should be kept as low as possible.
3. The actual physical properties of the textiles (pliability, texture, sheen, transparency, color) should be impaired as little as possible by the applied procedures. The restoration of these properties is another unique problem.
4. The reverse of the textile has to remain open for inspection by

specialists studying the weaving techniques.

5. The authenticity of the original must not be in any way impaired by the applied treatments.

Conservation Techniques

The techniques presently applied in the conservation of textiles have not been found satisfactory for archaeological specimens. There is no effective method for dealing with frayed edges and loose hanging threads. The back of the textile often remains covered in a permanent way. Also, the necessary reversibility is not assured. With the removal of the fixing agent (threads, glue) for any purpose, even only for changing the support, the textile is again reduced to its primary state of disintegration, or further deterioration. The amounts of applied chemical agents also need reconsideration.

First, the treatment of the textile object has been separated into two completely independent groups of operations:

1. Treatment of the textile object itself
2. Operations of mounting

These two groups are divided into several steps, all contributing to the final result. Each step has to be carried out by a different means, which should not affect the other steps. In this way, a better control of the whole treatment is assured, provided that the particular steps are not cumulated into more universal operations (e.g. consolidations, impregnation and mounting in one single operation). The sequence of the particular steps depends on the individual situation. Steps may sometimes be omitted when not necessary.

In the first process, dealing with the textile object itself, there are three basic steps:

1. Consolidation of threads, when there is a continuous loss of fibers, due to crumbling or to a fluffly condition of threads. The treatment is only local, mostly on threads that will have to be fixed in place, and no reversibility is expected. As consolidant a 0.01-0.1% solution of polybutyral methacrylate in toluene is applied very sparingly, only to moisten the threads. The extremely small amount of consolidant introduced will not affect the appearance of the textile.
2. Consolidation of weave, which is the most important operation for fragmentary textiles. It is only local, and generally is not considered as reversible, even when the fixing agent can be removed. The operation
has many purposes: repairing of tears and broken threads; making up for the loss of warp or weft; returning a dislodged thread back to its original position; joining separate fragments, and immobilizing the weave (for loosely woven textiles). Two basic techniques are used here:

1. Very minute droplets of glueing substance are put where necessary between threads with a thin dissecting needle, or
2. Thin new threads (silk on wool, linen on linen), are glued on the reverse, but, again, only as many as absolutely necessary.

The glueing substance does not penetrate to the surface and is practically invisible.

In both cases the amount of intervention is extremely small, and is without affect to the original properties of the specimen. It does help to keep together all precarious threads and separate fragments. As glues, the best yet found are the polyvinyl acetate and polymethacrylate emulsions of well adjusted thickness, giving small droplets but not allowing deep penetration. The threads have to be air-dry for the operation. See Figure 19.

Most textiles also need cleaning. It is, of course, best to clean first, before any operations are started. If this is not possible, and cleaning (washing) has to be carried out after the consolidation of the fabric, care must be taken to see that the previously applied consolidants are not washed out or harmed by the cleaning agent.

3. Protective impregnation concerns the textile as a whole, and has to be reversible (easy removal of impregnates, without dissolving the previously applied consolidants). Its purpose is to protect the textile against undue desiccation and biological agents. The products applied here may be soluble in water or in aliphatic hydrocarbons. Special attention must be given to disinfecting agents which, while destroying biological pests, may be even more harmful to the protected textiles.

In the second group of operations, dealing with mounting, there is no longer need to do anything substantial to the textile itself, but only to provide a background and support. These are fixed by mechanical means only and can be easily removed without the inconvenience of returning the textile to its initial fragmentary condition. As a rule, the background is prepared as a 'negative' of the original specimen, by cutting in the new material holes corresponding to the original and glueing an open net in these places. When the textile is laid on this negative, all missing parts and the
Figure 19. Consolidation of weave with droplets of glue, or with new threads glued on the left side of the textile: (1) neighbouring threads are joined together with droplets; (2) new thread is glued over to replace a missing fragment; (3) crossing ends are fixed with a droplet in between; (4) when selvedge is missing, the outer threads are fixed with droplets; (5) when the warp is missing (especially in Coptic textiles), the weft can be fixed with droplets; (6) loose hanging threads are fixed with a few threads put across; (7) loose inside threads are fixed in the same way as in (6); (8) the same as (5). The weft is kept in place with new threads; (9) tears are joined with a few threads glued across them; (10) loose fragments are joined to the main body with new threads; (11) a new thread is glued on the underside, all around the fragment, to protect the frayed edges and to immobilize the weave.

background are filled with the new material when viewing the front. The reverse, however, can be easily studied by looking through the net. The textile is fixed to the negative, in a manner which is invisible, by putting thin nylon threads (or another suitable material) over it. With textiles of not only documentary, but also highly decorative value, this system of an easily removable negative with necessary reconstructions may probably solve many problems without reconstructing directly on the original.

The purpose of the support is purely mechanical. It can be rigid or supple, flat or shaped, but it is never fixed permanently. The choice depends very much on the size and kind of textile. As a rule, sandwiching textiles between two transparent sheets should be avoided. Glass has alkaline properties. Synthetic sheets may give off injurious components, and have, moreover, the disadvantage of attracting dust. Additionally, the textile may become flattened and there is no possibility of adjusting the inner climate. 4

CHAPTER IV

DOCUMENTATION OF DETERIORATION OF MATERIALS: STUDIO THESIS WORK

The majority of fabric material is organic: vegetable or animal. Most processes associated with organic chemical systems are dynamic. The term denotes action, change of energy states, reactions constantly proceeding in one or more direction, balance or equilibrium maintained by forces always in motion. Textiles are subject to this dynamic mode of existence.

Natural deterioration of fibers begins as soon as they are removed from their natural habitat. It is incalculable to what extent fibers have oxidized and have been damaged by the process of preparing them into yarns and fabrics with coloring agents, and by their use since preparation. The actual condition is not always apparent to the eye. We notice deterioration after extended lengths of time and when fibers finally disintegrate to the point that we can no longer preserve them.

Kinetics deals with rates of reaction; from the standpoint of kinetics, the rate of oxidative change of a textile caused by atmospheric oxygen over a period of years is slow, whereas the rate of oxidation of the same article by fire is very rapid.

Organic reactions usually require two reactants, for example, a textile component plus oxygen; or special environmental conditions such as ultraviolet radiation, moisture, temperature, pressure; or a catalyst such as the enzyme action of certain microorganisms. Most of these reactions in textiles can be altered or slowed by removing a reactant from the field of reaction, by changing the environment, or by removing the catalyst. This is an oversimplification of what is involved as deteriorative changes may occur in a textile as a result of any of a great number of influences. A textile may be made up of several parts - a fiber component and a group of a few or several additive materials including: manufacturing coatings, colorants, soils, fungicides, insecticides, foreign matter it may have come in contact with, etc. Environmental factors: sun water, oxygen, wind, etc.,
may react directly on the fibrous component of the textile, on any of the several additives, and on the biological agents present on the textile. The biological agents may act upon the fiber and may act upon, or be acted upon, by the additives, which in turn may react in various ways with the fiber.

Considering the intent or use of a textile structure, not all reactions are undesirable. The reactions necessary for the setting of a resin on or in a textile are highly desirable, whereas the reactions which proceed toward the breakdown of the resin are certainly undesirable. The change in color from oxidation, which takes place as the penetrated fibers from the indigo dye vat come in contact with the air, is inevitable and desirable.

Every part of weaving: preparation, calculation, and manipulation - is a process. Deterioration of fibers and woven structures is a process also. It becomes apparent from use and age of a textile structure; it emerges as the object is in contact with the elements in its environment.

The process of deterioration of a textile structure as an art form was foremost in my thesis work. It was spontaneous, valuable as a creative media, and certainly a beginning, for me, into vast areas of unrealized substance, both artistic and scientific in fiber form.

The term permanence evokes ambivalent feelings. The pieces I present are not final. They will carry out their process of deterioration. This may result simply by an overzealous viewer poking his finger through one of the structures which may lead to ultimate disintegration. It is of consequence that this happens. Therefore, permanence in my artwork is not applicable. Dynamic change is.

This may seem incongruous with my research on textile conservation. It is not. Time and its relationship to states of matter is the key. My time is present, fast; my dynamic change takes place in minutes. It is immediately recognized. The dynamic change in a conserved textile is still present. It is only immensely magnified, taking place within an expansive, slowed, vast amount of time. My research reinforces the statement that when dealing with textiles, permanence is non-existent. Conservation cannot stop deterioration; it can only remove the object from the field of reaction.

As a result of study and research I gained a working vocabulary as to what would happen when a certain fiber was exposed to different means of deterioration. However, there is a tremendous lack of documented information
about specific situations in the deterioration of fabrics. Therefore, I only had a vague idea as to what would happen in my experimentation with woven structures.

I set up my own criteria. I prepared eight fabrics. These were all similar in construction. The only difference in the structures was that five were of cotton, three were of silk, one of the silk structures was woven in the color as it came off the cone, and the yarns of the rest were dyed different colors before woven. After weaving the structures, I painted their surfaces with Liquitex acrylic colors. The paint was applied over a coarse woven grid which left the opposite image of plain weave (minute squares) imprinted on the surface of the fabric. Each was ready to undergo a separate deteriorative process.

I am supplying photographs and technical information for the reader that was unable to view the weaving process, the deterioration process, and the works presented for exhibition.
Fabric #1

1. Fiber
   warp: 5/2 white Chalfin cotton; dyed
   weft: 5/2 white Chalfin cotton; dyed

2. Direction of Spun Threads
   S twist

3. Type of Weave
   tabby
   weft face

4. Count Per Inch
   warp: sett 10; 18 inches
   weft: 48 picks per inch; 22 inches
   reed: #10 at a single sley denting sequence

5. Presence of Selvages
   2 selvages; single sleyed
   2 sides rewoven and clipped (warp ends)

6. Applied Fiber Decoration
   none

7. Presence of Sewing Thread or Stitch Holes
   none

8. Presence of Colorants
   Direct Cotton Dye: W. Cushing and Co.
      "Perfection" Dye
      Ecru
      (Note: Glauber's Salts)
   Paint: Liquitex Acrylic Artists Colors
      Cerulean Blue       Payne's Gray
      Burnt Umber        Titanium White
      Burnt Sienna       Yellow Ochre
Plate 2. Deteriorated Fabric #1
9. Presence of Soils/Deterioration

Exposure to Soil

**objective:** It was my intention to bury this piece for 65 consecutive days and to note the effect of the cold ground conditions of a Rochester winter.

**description of actual deterioration process:**
The piece was buried January 15, 1977 in a barn structure where the soil, mixed with rotting timber, was not frozen solid but still received the chill from the extreme weather conditions occurring outside. It remained untouched under 18 inches of soil until March 22, 1977 when it was retrieved and examined.

**effects incurred:**
There was a clinging of dirt particles to the surface of the fabric. This indicates the beginning phase of deterioration by contact with soil. The cold weather conditions prevented the action of microbial growth and the rot of the cotton fiber. This will happen if temperatures are warm and moisture is present. There was no noticeable affect to the applied paints; they remained intact and without a change of color.
Plate 3. Fabric #2 Before Exposure
Fabric #2

1. Fiber
   warp: 5/2 white Chalfin cotton; dyed
   weft: 5/2 white chalfin cotton; dyed

2. Direction of Spun Threads
   S twist

3. Type of Weave
   tabby
   weft face

4. Count Per Inch
   warp: sett 10; 18 inches
   weft: 48 picks per inch; 22 inches
   reed: #10 at a single sley denting sequence

5. Presence of Selvages
   2 selvages; single sleyed
   2 sides rewoven and clipped (warp ends)

6. Applied Fiber Decoration
   none

7. Presence of Sewing Thread or Stitch Holes
   none

8. Presence of Colorants
   Direct Cotton Dye: W. Cushing and Co.
      "Perfection" Dyes
      Dark Brown and
      Navy Blue
   (Note: Glaubers Salts)
   Paint: Liquitex Acrylic Artists Colors
      Burnt Umber       Titanium White
      Burnt Sienna      Yellow Ochre
      Payne's Gray
Plate 5. Metal Plate After Exposure to Fabric #2
9. Presence of Soils/Deterioration
Exposure to Contact with Iron Plates

objective: My intention was to place a wet cotton fabric between two sheets of iron and note the effect that rusting would have upon the structure.

description of actual deterioration process:
I saturated the fabric completely with tap water and placed it between two flat sheets of iron. Within 24 hours rust began to form on the surface of the fabric. The piece was then left untouched for twenty days thus allowing it to dry completely. I resaturated the fabric again, allowed it to dry for twenty days and repeated this step once again before inspection and exhibition.

effects incurred:
The fabric had adhered itself to the metal sheets and was peeled away for inspection. The oxidation process of rusting had left a brilliant orange pattern on the surface of the structure. Not only did rust form but the firescale from the iron had transferred itself as an integral part of color and pattern on the fabric. The paint remained a permanent fixture, not changing in color. It only disappeared visually behind the rust covering. The iron plates became intriguingly patterned also; they mirrored the texture of the woven fabric and its rusted surface.
Plate 6. Fabric #3 Before Exposure
Fabric #3

1. Fiber
   warp: 5/2 white Chalfin cotton; dyed
   weft: 5/2 white Chalfin cotton; dyed
2. Direction of Spun Threads
   S twist
3. Type of Weave
   tabby
   weft face
4. Count Per Inch
   warp: sett 10; 18 inches
   weft: 48 picks per inch; 22 inches
   reed: #10 at a single sley denting sequence
5. Presence of Selvages
   2 selvages; single sleyed
   2 sides rewoven and clipped (warp ends)
6. Applied Fiber Decoration
   none
7. Presence of Sewing Thread or Stitch Holes
   none
8. Presence of Colorants
   Direct Cotton Dye: W. Cushing Co.
      "Perfection" Dyes
      Rust and
      Terra Cotta
   (Note: Glaubers Salts)
   Paint: Liquitex Acrylic Artists Colors
      Cerulean Blue   Payne's Gray
      Burnt Umber    Titanium White
      Burnt Sienna   Yellow Ochre
Plate 7. Deteriorated Fabric #3
9. Presence of Soils/Deterioration
Exposure to Fire

**objective:** It was my intention to subject areas of a cotton fabric to an open flame and to note the effects of oxidation while burning.

**description of actual deterioration process:**
When the fabric came in contact with a flame it did not ignite immediately as paper would. I attribute this to the density of the woven structure. The area in contact with the flame first began smoking, and turned gray in color. As it blackened it also burst into flame. It began to burn by itself slowly, increasing its rate as the flame consumed a larger area, but never burned rapidly. The edge of the burning fabric would glow and curl making an ash and having the same characteristic smell of burning paper. When an area burned completely the warp threads disintegrated before the weft threads.

**effects incurred:**
The partially burned areas had lost all strength, was torn easily and eventually fell apart when handled. The applied polymer paints changed color slightly at first and almost disappeared as the fabric blackened. Surprisingly they became intense in color just before the structure would disintegrate.
Fabric #4

1. Fiber
   warp: 5/2 white Chalfin cotton; dyed
   weft: 5/2 white Chalfin cotton; dyed
2. Direction of Spun Threads
   S twist
3. Type of Weave
   tabby
   weft face
4. Count Per Inch
   warp: sett 10; 18 inches
   weft: 48 picks per inch; 22 inches
   reed: #10 at a single sley denting sequence
5. Presence of Selvages
   2 selvages; single sleyed
   2 sides rewoven and clipped (warp ends)
6. Applied Fiber Decoration
   none
7. Presence of Sewing Thread or Stitch Holes
   none
8. Presence of Colorants
   Direct Cotton Dye: W. Cushing and Co.
      "Perfection" Dyes
      Roseda Green, Dark Brown, Black, and Navy Blue
   (Note: Glaubers Salts)
   Paint: Liquitex Acrylic Artists Colors
      Cerulean Blue       Payne's Gray
      Burnt Umber         Titanium White
      Burnt Sienna
9. Presence of Soils/Deterioration
   Exposure to Sodium Hypochlorite 5% (Clorox) Bleach

   **objective:** It was my intention to pour Clorox Bleach, a liquid used and found in most households, directly onto the fabric and to note the damage incurred with several applications.

   **description of actual deterioration process:**
   I poured the bleach in concentrated areas on to the outstretched piece of fabric and waited for it to naturally wet the cloth. Once it had saturated an area, discoloration began. The royal blue color turned gray, then a deep yellow, and as it began to turn a light yellow, I thoroughly rinsed the structure. I placed it in the extractor, steam pressed it and laid it flat to dry. The following day I resaturated an area, leaving the bleach in the fabric.

   **effects incurred:**
   The area saturated once and rinsed thoroughly turned a deep yellow brown; the area where the bleach was not rinsed lightened to a bright yellow. The bleaching action had no effect on the polymer paints.
Plate 10. Fabric #5 Before Exposure
Fabric #5

1. Fiber
   warp: 5/2 white Chalfin cotton; dyed
   weft: 5/2 white Chalfin cotton; dyed
2. Direction of Spun Threads
   S twist
3. Type of Weave
   tabby
   weft face
4. Count Per Inch
   warp: sett 10; 18 inches
   weft: 48 picks per inch; 22 inches
   reed: #10 at a single sley denting sequence
5. Presence of Selvages
   2 selvages; single sleyed
   2 sides rewoven and clipped (warp ends)
6. Applied Fiber Decoration
   none
7. Presence of Sewing Thread or Stitch Holes
   none
8. Presence of Colorants
   Direct Cotton Dye: W. Cushing and Co.
   "Perfection" Dyes
   Copenhagen Blue,
   Navy Blue and
   Silver Gray
   (Note: Glaubers Salts)
   Paint: Liquitex Acrylic Artists Colors
   Cerulean Blue   Titanium White
   Burnt Umber    Burnt Sienna
Plate 11. Deteriorated Fabric #5
9. Presence of Soils/Deterioration
Exposure to 100% Nitric Acid

objective: It was my intention to subject the cotton fabric to an unusually harsh acidic situation and to note how drastic the results would be not excluding complete destruction.

description of actual deterioration process:
I very slowly and carefully poured nitric acid onto the structure. It was a cold solution but of 100% strength. The fabric turned purple-blue in color where the acid came in contact with it. There was no color change of the paints applied. After 30 seconds a vapor appeared and began rising from the structure. I exposed this piece to the 100% acid solution for 5 minutes and then rinsed it thoroughly. I put it in the extractor and placed it flay to dry overnight. The proceeding day I washed the fabric in the washing machine and steam pressed it dry.

effects incurred:
The effect was one of discoloration to the dyed fiber; the paint color remained constant. The acid had no effect on the strength of the fabric; no holes appeared after washing.
Fabric #6

1. Fiber
   warp: natural 2 ply contessa silk; dyed
   weft: natural 2 ply contessa silk; dyed

2. Direction of Spun Threads
   Z twist

3. Type of Weave
   tabby
   weft face

4. Count Per Inch
   warp: sett 10; 18 inches
   weft: 56 picks per inch; 22 inches
   reed: #10 at a single sley denting sequence

5. Presence of Selvages
   2 selvages; single sleyed
   2 sides rewoven and clipped (warp ends)

6. Applied Fiber Decoration
   none

7. Presence of Sewing Thread or Stitch Holes
   none

8. Presence of Colorants
   Direct Cotton Dye: W. Cushing and Co.
      "Perfection" Dyes
      Mummy Brown and
      Egyptian Red
   Paint: Liquitex Acrylic Artists Colors
      Cerulean Blue   Titanium White
      Burnt Umber     Yellow Ochre
      Burnt Sienna
Plate 13. Deteriorated Fabric #6
9. Presence of Soils/Deterioration
Exposure to 100% Nitric Acid

objective: It was my intention to subject this silk structure to 100% nitric acid. I knew this acid to be one of the most destructive. I had seen it take little effect on the cotton fabric. How would it effect silk?

description of actual deterioration process:
After placing the structure on the counter top, I very slowly and carefully poured 100% nitric acid onto the silk. Immediately it turned the fabric a deep purple color and a vapor formed. Within two minutes the exposed area turned a bright orange, began bubbling, and appeared fluid. I rinsed the fabric thoroughly.

effects incurred:
The areas of longest penetration dissolved completely while areas of a shorter exposure did not dissolve completely but resolidified into a crusty weakened brittle surface. The areas of shortest exposure remained discolored only. The acid changed the color of each pigment in the partially dissolved areas. It remained permanent in the areas of least exposure. I chose to exhibit the back side of this piece for purely aesthetic reasons.
Plate 14. Fabric #7 Before Exposure
Fabric #7

1. Fiber
   warp: natural 2 ply contessasilk
   weft: natural 2 ply contessa silk
2. Direction of Spun Threads
   Z twist
3. Type of Weave
   tabby
   weft face
4. Count Per Inch
   warp: sett 10; 18 inches
   weft: 56 picks per inch; 22 inches
   reed: #10 at a single sley denting sequence
5. Presence of selvages
   2 selvages; single sley
   2 sides rewoven and clipped (warp ends)
6. Applied Fiber Decoration
   none
7. Presence of Sewing Thread or Stitch Holes
   none
8. Presence of Colorants
   Paint: Liquitex Acrylic Artists Colors
   Titanium White
   Cerulean Blue
   Burnt Umber
9. Presence of Soils/Deterioration
Exposure to Fire

objective: My intention was to expose the silk fabric to fire and to compare how it burned to the way a cotton piece already exposed to fire burned. Noting the differences clarified, for me, the identification of fibers by burning.

description of actual deterioration process:
The silk structure was held over a burner having a constant flame. First it turned brown and began smoking, smelling of singed hair. With continued burning it turned black and formed silver gray ashes. The silk fabric itself never burst into flame. The burning area always extinguished itself when removed from contact with the flame.

effects incurred:
The areas burned were blackened with brown rings around their periphery. The paint applied disappeared. These blackened areas when touched crumbled into ashes. In the areas of extended burning, holes appeared without any physical abrasion.
Plate 16. Fabric #8 Before Exposure
Fabric #8

1. Fiber
   warp: natural 2 ply contessa silk; dyed
   weft: natural 2 ply contessa silk; dyed

2. Direction of Spun Threads
   Z twist

3. Type of Weave
   tabby
   weft face

4. Count Per Inch
   warp: sett 10; 18 inches
   weft: 56 picks per inch; 22 inches
   reed: #10 at a single sley denting sequence

5. Presence of Selvages
   2 selvages; single sley
   2 sides rewoven and clipped (warp ends)

6. Applied Fiber Decoration
   none

7. Presence of Sewing Thread and Stitch Holes
   none

8. Presence of Colorants
   Direct Cotton Dye: W. Cushing and Co.
      "Perfection" Dyes
      Dark Brown and
      Navy Blue

   Paint: Acrylic Artists Colors
      Titanium White  Burnt Umber
      Cerulean Blue  Burnt Sienna
Plate 17. Deteriorated Fabric #8
9. Presence of Soils/Deterioration

Exposure to Mureatic Acid

**objective:** It was my intention to pour mureatic acid onto the silk fabric and to note the effects incurred making comparisons with the previous experiments using acids.

**descriptions of actual deterioration process:**
I carefully poured mureatic acid onto limited areas of the fabric. Only a slight vapor formed and dissipated. Where the acid came in contact with the structure, it immediately turned a brilliant purple color and began contracting the fibers forming lakes of fluid and hills of untouched fabric. This produced a three dimensional structure. No further change became apparent. I placed the silk piece in the bottom of the sink allowing the acid to dilute and spread for a short period of time over the entire surface. It was then thoroughly rinsed and placed in the extractor.

**effects incurred:**
When dry, the piece appeared a very deep purple where the valleys formed. The surrounding areas turned a light shade of purple from contact with the diluted solution. There was a total color change in the fabric. The applied paint maintained its original color.
Conclusion

The importance and vitality of my thesis work lies in the experience itself. The excitement is in the process. The experience is one of direct presence, thus the exhibition pieces are unsentimental. They are a universal visual definition of the physical properties of specific materials and their breakdown.

It is beyond self-expression. The ideas seem to be fixed in reality but they are not really certain. They represent the point where human reason and nature meet each other. It is an activity which eventuates a product that is not sacred ... it is either kept or thrown away.

It is important for me to deal with unknowns. Repetition is fatal. Change is the only constant. It is the source of new experience, images, and growth.

The excitement generated during my thesis work is evidence that it was unprecedented or not repetitious of any work I have done previously. However, there have been sequences of progression. This is attributed to change.

In my lifetime these experiences are foremost in advancing myself as an individual and contributing member of society. However, many centuries from now those experiences will be forgotten. The work will stand and defining it will be history's job.
GLOSSARY

Acetyl: the univalent radical CH$_3$CO, of acetic acid.

Acetylated: to introduce an acetyl group into (the molecule of an organic compound), as by treatment with acetic anhydride.

Atom: the smallest unit into which an element can be divided and still maintain its identity as an element.

Aliphatic (hydrocarbons): designating a large class of saturated or unsaturated hydrocarbon compounds of the open-chain formation, including the alkanes, alkenes, and alkynes.

Amino acid: any group of organic compounds containing the amino group (NH$_2$ group combined with a nonacid radical) combined with the carboxyl radical and forming an essential part of the protein molecule.

Amphoteric: exhibiting the characteristics of both an acid and a base; (amino acids) one end is acidic because of an acid-carboxyl group - COOH, while the other end is basic because of an amine group - NH$_2$. The acid group ends can react chemically with the basic end of another amino-acid.

Auxochrome: any of certain radicals that will convert a chromophore into an acidic or basic textile dye.

Azo: containing nitrogen.

Beta napthol: an isomer of naphol, used in the manufacture of dyes.

Catalyst: any substance that causes catalysis; an increase in the rate of chemical reaction, caused by the presence of a substance that is not permanently altered by the reaction.

Chelation: the inactivation of metallic ions in a solution by an organic reagent with whose molecules the metallic ions are strongly bound in a relatively inactive ring structure.

Chemistry: the study of the properties and composition of matter, and of the changes or transformations that matter undergoes.

Chromophore: a group of atoms or electrons so linked within a molecule as to produce certain colors when combined under proper conditions.

Colloid: a state of matter in which finely divided particles of one substance (the disperse phase) are suspended in another (the dispersion medium) in such a manner that the electrical and surface properties acquire special importance.

Compound: two or more combined elements.

Diazotize: to bring about chemical reactions or changes that form a diazo compound or derivative, any of a group of compounds in which two nitrogen atoms are united to a hydrocarbon radical.

Distend: to expand or enlarge by pressure from within.

Elements: the practical limits of chemical analysis, or substances incapable of decomposition by any means with which we are at present acquainted.

Emulsify: to make into an emulsion - a colloid system, consisting of the particles of one liquid finely dispersed in another.
Endothermic: pertaining to, attended by, or produced from the absorption of heat.

Ester: any of a class of organic compounds formed by the reaction of an acid with an alcohol, with the elimination of water.

Exposure (to light): proportional both to illumination value and to time of exposure, to lux multiplied by time, or lux-hours. \( 1 \text{ Mlxh} = 1 \text{ million lux hours} \).

Fugitive: fading of dye color.

Hygroscopic: materials that are very water-absorbent; the ability of a fiber to take up moisture and is expressed in terms of moisture regain, which is the percentage of moisture that a bonedry fiber will absorb from the air under standard conditions of temperature and moisture.

Illumination value: strength of visible light as it appears to the human eye, measured in lux (lumens per square meter), foot candles (USA) lumens per square foot.

Inhibitors: chemicals used for slowing down the reaction.

Isomer: one of two or more compounds identical in composition, but having different structural arrangements and exhibiting different properties.

Ketone: one of a class of organic compounds in which the carbonyl radical unites with two hydrocarbon radicals. The simplest member being acetone.

Leuco: white, lacking color.

Molecule: a group of atoms, two or more of the same or different elements may combine to form a molecule.

Mixture: matter which varies in homogeneity and composition. Homogenous means it is of the same composition, the opposite is heterogenous.

Naptha: a volatile, colorless petroleum distillate intermediate between gasoline and benzene, used as a solvent, cleaning fluid, fuel, etc.

Napthol: either of two isometric compounds \( C_{10}H_{8}OH \), derived from naphthalene and used in making dyes; any of a class of naphthalene derivatives containing the hydroxyl group.

Peptization: the process of maintaining the separation of fine particles within a liquid.

Phenolic: containing phenol, a white crystalline, caustic compound, \( C_{6}H_{5}OH \), with a characteristic odor, derived from coal tar and used as a disinfectant; also called carbolic acid; any series of aromatic hydroxyl derivatives of benzene or its homologs.

Photo-oxidation: photodegradation; fading of a dye or weakening of a fabric from exposure.

Polymerization: the process of changing the molecular arrangement of a compound so as to form new compounds having the same percentage composition as the original, but of greater molecular weight and different properties.

Plasticizers: chemicals used to control stiffness.

Properties: characteristics by which one kind of matter may be distinguished from or compared with other kinds of matter.
Relative humidity: RH; actual amount of water vapor in air, divided by the maximum amount of water vapor in air, divided by the maximum amount which the air could hold at that temperature, multiply by 100 = percentage of relative humidity of air.

Saponify: to convert (a fat oil) into soap by the action of an alkali; to decompose into an acid and an alcohol; alkalis have the property of attacking certain fats, oils and greases to convert them into soluble soaps.

A scientific law: not the final, ultimate answer, but the best explanation of the present facts, and it is open to revision as new information is found.

Sequestrant: a chelating agent.

Solubilization: when a soil, such as an oil or grease, does not dissolve in water. Upon adding a very small amount of detergent to the water, the oil is first dissolved in the detergent which in turn is dispersed in the form of very small micellar complexes within the water.

Specific gravity: the ratio between the density of a liquid (or object) with that of water at the same temperature (water: 1g/ml at 4 C).

Substance: matter which is homogeneous and has an exact composition. Homogeneous is of the same composition, uniform, throughout. A substance may either be an element or a compound.

Substrate: surface to be acted upon by the surfactant, the wetting agent.

Sulfonate: to form a sulfonic acid; to subject to the treatment of sulfonic acid.

Sulfonic acid: any substance of several compounds having an organic radical in combination with the sulfonic radical SO₂OH, used in organic synthesis.

Surfactant: surface active agents.

Syndets: synthetic detergents.

Tendering: decrease in strength.

Tinctorial: of or pertaining to coloring, dyeing, imbuing with color.

Titer: a way of comparing the melting points of the fatty acid or mixture of fatty acids that compose soap.

Trivalent: having a valence or combining value of three.

Turgid: unnaturally distended, as by contained air or liquid swollen, inflated.

Valence: the property possessed by an element or radical of combining with or replacing other elements or radicals in definite and constant proportion; the number of atoms of hydrogen (or its equivalent) with which an atom or radical can combine, or which it can replace.

Volatile: evaporating rapidly at ordinary temperatures on exposure to the air. Capable of being vaporized.
BIBLIOGRAPHY


