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IMAGE MECHANISMS IN SCREENLESS LITHOGRAPHY

by

Charles E. Martin

A thesis submitted in partial fulfillment of the
requirement for the degree of Master of Science in the
School of Printing in the College of Graphic Arts and Photography
of the Rochester Institute of Technology

June, 1975

Thesis adviser: Dr. Julius L. Silver

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An Abstract

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ABSTRACT

In conventional lithography, a halftone screen is used to photographically convert the continuous-tone image of the original into a grid of very small, closely spaced dots of constant density but varying areas. Screenless or continuous-tone lithography is a printing process capable of reproducing images with gradated tones without the use of a halftone screen. Screenless lithography has a high quality potential because it has few of the inherent problems that limit the quality of the halftone process.

This thesis investigates the image mechanisms in screenless lithography and in particular the role of variable water receptivity. It was hypothesized that in screenless lithography which uses a particular image carrier known as the Association Products plate, the continuous-tone image is due to selective emulsification of the ink resulting in a varying ink layer thickness and therefore varying densities. It was theorized that the plate has a water receptivity which varies with exposure to light and that this results in varying degrees of water-in-ink emulsification when the plate is dampened and inked. When transferred to paper and dried this results in an ink layer of varying thickness, which in turn causes a variation in optical density.

A mathematical relationship was developed relating optical density, percentage of emulsified water, and ink layer thickness. This relationship allowed prediction of the amount of water-in-ink emulsification necessary to produce a given density range and a prediction of the amount of emulsification expected on a given plate area associated with a particular printed density.

Testing proved that these predicted values were not present in actual printing from the plates. It was concluded that the hypothesis is invalid.

Abstract approved: ______________________________, thesis adviser

______________________________, title and department

______________________________, date

CHAPTER I

INTRODUCTION

Screenless Lithography

Screenless or continuous-tone lithography is a printing process for reproducing images with gradated tones without the use of a halftone screen. In conventional lithography, a halftone screen is used to photographically convert the continuous-tone image of the original into a grid of closely spaced dots of constant density but varying areas which give the illusion of tone gradation.

Although there has been a continuing interest in screenless processes since the earliest days of lithography, plate developments in the past two decades have given a new impetus to this interest. Screenless lithography has a very high quality potential because it has few, if any, of the inherent problems that limit the quality of the halftone lithographic process.

Early Screenless Processes

Screenless lithography with bitumen on stone

Although it is a common misconception that screenless lithography was first attempted in the mid-1950's, its beginnings were actually a century sooner. In fact, the reproduction of continuous-tone images by lithography preceeded the introduction of the screened halftone process by almost thirty years. The first successful attempts at screenless lithography were made in 1852 by Lemercier, a famous Paris lithographer, in collaboration with Barreswil and Davanne, chemists and amateur photographers, and Lerebours, a well known photographic optician. Based on the methods of Joseph Nicephore de Niepce, they coated a grained lithographic stone with a solution of bitumen of Judea[1] in ether. After exposure under a continuous-tone negative, the stone was washed in turpentine, etched with acid, inked, and then printed using the standard lithographic procedures of the period. In 1854 they published a now very rare collection of these direct asphalt photolithographs. These prints were said to show remarkable strength with a somewhat coarse grain in the middle tones.[2]

Others soon adopted and improved Lemercier's process, especially Karl von Giessendorf of the Government Printing Office in Vienna who in the late 1850's introduced the process to the lithographic plant of Reiffenstein and Rosch. In 1866 Reiffenstein produced photolithographic prints in color by this method. A later improvement called the "Orell-Fussli process" also employed the grained bitumen stones for color photolithographic printing. It is said that enormous editions were produced by this method. [3]

Screenless lithography with bichromated gelatin

In 1855 a French chemist and engineer, Alphonse Louis Poitevin, introduced a method of screenless lithography which was entirely different from that of Lemercier. The lengthy exposure times and the washing with turpentine, which at the time was rather expensive, had hindered the spread of Lemercier's method. Poitevin's method was to prove more certain, required shorter exposures and needed only water for washing. It would soon replace the bitumen process. Fox Talbot had discovered three years earlier that mixtures of potassium bichromate with gelatin were light sensitive. Poitevin devised a process of printing pictures from continuous-tone negatives using greasy ink transferred from a layer of bichromated gelatin. The layers were coated on a lithographic stone. After exposure through the negative, washing, drying and again dampening, he inked the stone and obtained an image in gradations of tone. The image was subsequently transferred to paper.

Because his gelatin layer was coated on a lithographic stone and was imaged photographically, he called his process "photo-lithography." This was not, however, the beginning of the currently popular printing process of photolithography. It was later recognized that his process differed significantly from the lithography of that period, as the stone acted merely as a support for the printing surface. The process was more accurately renamed "photo-collographic" and eventually became known as "lichtdruck" in the German speaking countries and "collotype" or "photo-gelatin printing" in the English speaking countries.[4] Collotype subsequently attracted some of the brightest printing experimenters of the nineteenth century, and by the late 1800's it had become one of the most important of the photomechanical processes. Collotype gained this position primarily because of its exceptional quality and tonal capabilities. It was widely practiced throughout Europe and later in the United States. Its principles were also applied to several processes for transferring unscreened images to lithographic stones and zinc plates for subsequent screenless printing. Collotype was unquestionably the most important of the nineteenth century screenless processes.

The decline of the early processes

Although all of these early methods of screenless tone reproduction achieved some degree of success even after the introduction of the screen halftone process, they all suffered from a common deficiency. They required a great deal of attention to detail and a great deal of skill. Without this skill and careful manipulation, the image quality deteriorated and the processes became unreliable and unpredictable. The introduction of the halftone process provided a solution to these problems. As it evolved, the halftone process became more reliable and more predictable, and as materials were improved, and systematic procedures developed, relatively less skill was required on the part of its practitioners. Because of this, it quickly replaced the "screenless" processes as the preferred method for tone reproduction. With over one hundred years of continuing research and development, the halftone process has today reached a degree of effectiveness probably unimagined by its inventors. In fact, such extensive research has been done that the process may have neared the limit of its quality potential. The remaining deficiencies in the halftone process are mostly inherent, being caused by the presence of the dots themselves, thus seriously limiting further improvements.

Modern Screenless Processes

In the early 1950's the realization of the limitations of the halftone process plus the need for a high resolution process for reproducing aerial photographs and photomaps, led to a renewal of interest in screenless lithography.

Collotype improvements

This interest resulted in an attempt to increase the run lengths obtainable from collotype plates. Under contract to the U. S. Corps of Engineers, Harry H. Lerner developed an offset collotype plate which he claimed would produce in excess of 25,000 copies without any appreciable loss in quality. The plate coating was bichromated gelatin with small amounts of water soluble dialdehydes or ketoaldehydes. Before printing, the plates were treated with a glycerin-formaldehyde solution. These additives increased the toughness of the gelatin layer. The plates were used on a standard offset press with the dampening system removed and plate dampening provided by high room humidity as in conventional direct collotype.[5] Apparently the process was not completely perfected, as no commercial applications were made.

Diazo compounds on grained aluminum

In 1951, the first presensitized, positive-working plates were introduced to the U. S. market. These plates were grained aluminum, coated with a diazo oxide type of coating. It was soon discovered that careful exposure and processing would yield on the plate a number of distinct steps from the stepped gray scales used as exposure guides. This came to the attention of the Graphic Arts Technical Foundation, and in 1958 they produced and evaluated both single and four color screenless printing from these plates.[6]

In 1961, a new positive diazo oxide wipe-on plate was introduced by the Sumner Williams Company. These plates had a very deep grain produced by dry blasting the aluminum substrate. They exhibited even greater continuous-tone characteristics than the presensitized plates. A number of experimenters produced excellent single and multicolor work using these plates.

Association Products plates

In 1969 Dr. Julius L. Silver presented a paper to the Technical Association of the Graphic Arts on "Photosensitive Association Products." He described these materials as "eminently suitable as photo-lithographic printing plates in general, including screenless printing plates." These plates are of a completely different nature than the diazo plates previously described. The term association product refers to a combination of materials which are bonded physically rather than chemically. Such combinations frequently exhibit properties different than the mere average of their components. In the case of the Association Products printing plate, the materials are an ethylene oxide polymer and a phenolic resin. The resulting Association Product is a tough, flexible, thermoset, and hydrophilic material. The addition of a suitable photo-sensitizer causes the normally hydrophilic material to be transformed to an oleophilic state in direct proportion to the action of ultra-violet radiation. The plates consist of a single homogeneous coating which contains both the image and non-image areas with no exposed substrate. Excellent examples of screenless lithography have been produced from these plates.

Screenless Process Potential

Quality advantages

Research to date has shown the quality potential of screenless lithography to be exceedingly high. Most of this derives from the fact that it has few of the inherent problems that limit the quality of the halftone process. Among these problems are the following:

Resolution

Resolution is the ability of the printed image to reproduce fine detail or closely spaced lines. Obviously detail finer than the spacing between dots cannot be reproduced. While screenless images also have a limit to their resolving power, they are capable of much higher resolution. High resolution is of special importance in areas of printing such as aerial mapping, scientific and technical illustrations, fine art reproductions and microprinting.

Moire'

Moire' is the interference pattern that results when two halftone images are superimposed. Although this is usually a problem only in multicolor halftone printing, moire' can also occur between the halftone screen and a recurring pattern in the image itself.

Mid-tone jump

When the corners of adjacent dots join, an abrupt change in density occurs. In square-dot halftone screens this occurs at or near the 50 percent dot area as the four corners of each dot join simultaneously. Elliptical dot screens have improved on this problem because elliptical dots join in only two corners at a time. Even though this results in two density jumps, the net effect is less noticeable.

The above problems relate to both single and multicolor printing. There are other inherent halftone deficiencies that relate primarily to process color printing. These include:

Grey balance.

In halftone printing, equal ink areas of magenta, cyan, and yellow will not produce a neutral gray as would be expected. Instead, equal areas will produce a brownish tone. To correct for this a larger dot area of cyan is normally used.

Proportionality failure

Individual dots surrounded by white paper produce an integrated color which appears weaker and less saturated when compared with a continuous-tone printing of the same color. This failure is more prevalent with magenta and cyan inks. Without correction, these inks when printed as halftone dots reproduce the lighter tones of the original as gray, less saturated colors.

Economic advantages

There are also certain potential economic advantages to screenless lithography, the most obvious being that no halftone screening step is required. Assuming that they possess the proper density range, it is possible to go directly from the original negatives or positives (or the separation negatives or positives) to the plate, thus saving time and requiring less equipment. Further economies could result from the need for less color correcting. And theoretically no black printer would be necessary, requiring one less negative or positive, one less plate, and one less press run.[9]

Process problems

The above are only potential quality and economic advantages and in order for them to be fully realized a great deal of research is needed. The variables of the system, their relative significance, and their effects must be determined and then means of controlling and optimizing these variables established. Some of the currently recognized major problems of screenless lithography are: the range of densities in the negatives or positives which the plate will accept is usually quite limited, plate exposure latitude is very narrow, plate sensitivities are frequently inconsistent, and plate performance is frequently inconsistent and unpredictable.

Area of Investigation

Potential Areas

There are a number of areas in screenless lithography that are worthy of scientific investigation as well as offering possibilities for improving the process. For example, there are a great many variables in the process whose significance and effects are not well understood. Among these are variables of the plates such as substrate material and composition, coating compounds, sensitizers and the methods and conditions of their application to the substrate, and the plate exposure, handling and processing. Also of importance are the variables of printing such as inks, fountain solutions, blankets, press speeds, temperature, humidity, etc.

It would no doubt be worthwhile to investigate these variables, determine their significance and effects, and attempt to optimize them. An area that is, however, more basic and therefore potentially more worthwhile to the future of screenless lithography is the question of the mechanism of image formation.

Types of Lithographic Plates

Lithographic printing plates may be grouped into two broad categories depending on the nature of their image and non-image areas. The distinction between these two categories is important to the mechanism of image formation. Plates in which the image and non-image areas are of the same material are termed single-phase. In these plates no significant amount of the coating is removed during processing, and the coating thickness is relatively uniform between the image and non-image areas. The ability of the plate to selectively accept ink in the image area is usually due to some chemical or physical change in the coating material, rendering it oleophilic in the image area and hydrophilic in the non-image area.

Two-phase lithographic plates are those in which two different materials are used to form the image and non-image areas. Typically, in a positive working plate, the first material, the plate coating, is selectively solubilized during exposure and removed in the non-image areas during processing. This reveals the second material, usually the plate substrate itself, which then forms the hydrophilic non-image areas.

Types of Screenless Images

Regardless of the type of plate being used, any screenless or continuous-tone image produced by lithography must be of one of the following types even though plates capable of producing each of these types of image do not necessarily exist.

Variable image area

The image may not in fact contain continuous-tones but rather be a two-tone image consisting of very small, randomly spaced ink receptive areas varying in size to give the illusion of tone. These random areas might be the result of some surface characteristics of the plate, some surface characteristics of the plate substrate, variations in the coating thicknesses, pigment grains in the ink, or the grain of the continuous-tone negatives used to expose the plate.

Variable ink layer thickness

The image may truly be continuous-tone, consisting of an ink layer of varying thickness resulting in a varying optical density and hence varying tones. The varying layer thickness might be the result of various areas of the plate, depending on exposure, having varying degrees of ink receptivity and thereby accepting and transferring varying ink layer thicknesses to the paper.

Another possible cause of a varying ink layer thickness might be variable water receptivity. Various areas of the plate might accept varying amounts of water depending on exposure. This could perhaps affect ink transference resulting in an ink layer thickness which varies with exposure. Or the variable water receptivity could result in varying emulsification of the ink, producing upon drying, various ink layer thicknesses.

Combination effects

Both of the above could be acting together to form the image. It might be analagous to halftone gravure in which the image is formed from dots that vary in both area and ink layer thickness.

Thesis Objective and Hypothesis

The objective of this thesis is to investigate the role of variable water receptivity in the mechanism of image formation in screenless lithography. It is hypothesized that in certain types of screenless lithography, such as that produced using single-phase plates of the Association Products type, the continuous-tone image is due to selective emulsification of the ink, resulting in a varying ink layer thickness and therefore varying densities. This hypothesis implies that the various tonal values of the image are due to an ink layer of varying thickness. It is further implied that this varying thickness is due to the plates having a water receptivity which varies with exposure, resulting in a varying water-in-ink emulsification on the plate when it is dampened and inked. When transferred to paper and dried, this results in an ink layer of varying thickness, which in turn causes a variation in optical density or tone.

FOOTNOTES FOR CHAPTER I

[1] Bitumen of Judea, sometimes called "Syrian Asphalt" is a naturally occurring substance which is regarded as a fossilized resin. It is a black, brittle substance which can be pulverized into a brown powder. It may be resolved by means of differential solution into three substances, the third of which, known as "washed bitumen," is sensitive to light.

[2] Josef Maria Eder, *History of Photography*, trans. Edward Epstean (New York: Columbia University Press, 1945), p. 609.

[3] Ibid., p. 611.

[4] Charles W. Gamble, *Modern Illustration Processes*, 2d. ed. (London: Pitman and Sons, 1938), p. 217.

[5] Harry H. Lerner, Results of a Study on Offset Collotype," *Technical Association of the Graphic Arts, Proceedings of the Sixth Annual Technical Meeting* (1954), p. 29; and Harry H. Lerner, "Emulsion Coating and Method of Preparation," U. S. Patent 3,012,886 (1961).

[6] Frank Preucil, "New Materials and Methods for Color Reproduction," *Graphic Arts Technical Foundation, Reports of Progress During 1958* (1959).

[7] Julius L. Silver, "Photosensitive Association Products," *Technical Association of the Graphic Arts, Proceedings of the Twenty-First Annual Technical Meeting* (1969), p. 141.

[8] Ibid., pp. 142-147.

[9] Robert J. LeFebvre, "Continuous Tone Lithography," *Printing Impressions* (July 1966): 67.

CHAPTER II

LITERATURE REVIEW AND THEORETICAL BASES

The Mechanism of Image Formation In Two-Phase Plates

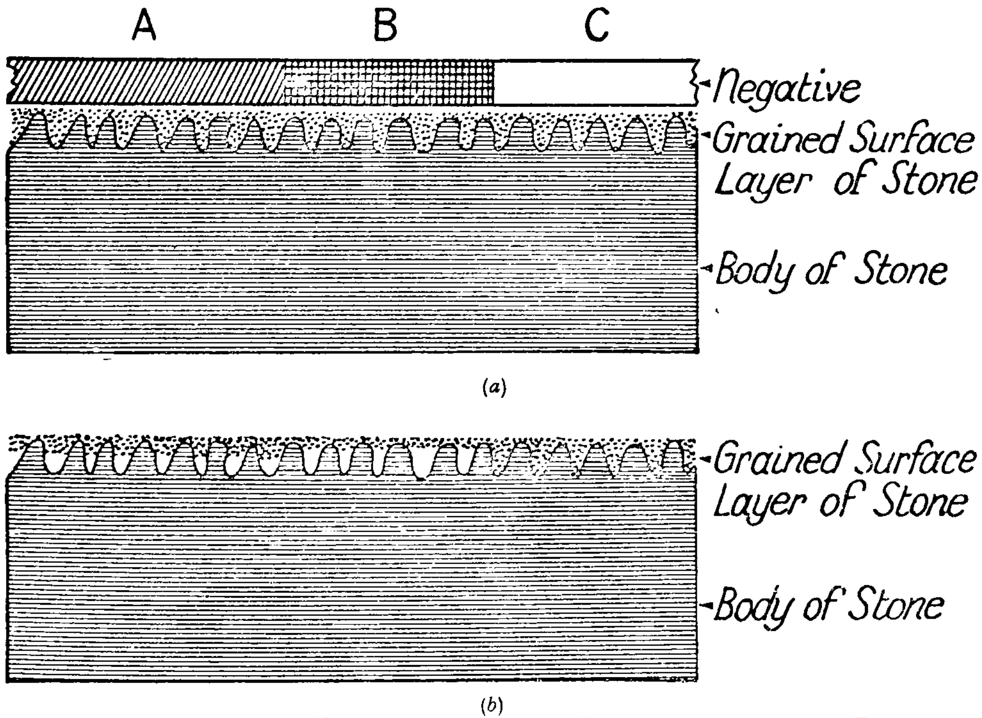
Bitumen on Grained Stone

The prints produced by all of these processes have an irrregular grained image produced by randomly spaced, irregularly shaped ink spots of varying area but constant density. It should be remembered that the lithographic stones used for the printing of line images had a very fine grain or essentially smooth surfaces. The stones used by the early practitioners of screenless lithography were not smooth but deeply grained, and this grain was essential to the formation of the image. The mechanism of image formation was reasonably well understood as the following quotes and accompaning illustration from two early writers will indicate.

> In the process where a continuous-tone negative is employed, the surface receiving the sensitive coating is not smooth but is "grained" - and the grain is deep - with the consequence that the film is not uniform in thickness but varies from one grain to another, and from one part of the same grain to another part. Consider now what would be the effect of exposing such a sensitive surface under a continuous-tone negative, a negative the tones of which have different degrees of opacity and, therefore, transmit different amounts of light. We have a film upon the deeply grained stone, a condition suggested in (the figure). . . It will be seen that the bitumen covers the top of the grains all over the surface to a slight extent. Above is the negative, where A is the medium tone, B more opaque, and C quite transparent, so that in a given time of exposure a certain amount of light has passed through A, not quite so much through B, but more through C, because it is transparent. Now let us assume that the time of exposure has been such that the coating under C has been wholly changed, so that down

to the bottom of the cavities the whole of the bitumen has been altered. Then, because there has not been so much light passed through A there will not be so much bitumen changed and there will be still less under B. Say, that under A it has changed through one-half of the thickness, and under B to one-quarter of the thickness. Now let us consider the next stage, when the film has been subjected to the action of the dissolving turpentine. The unchanged parts dissolve away, leaving the insoluble, that is, the changed, bitumen behind.

Now, apparently, the whole surface of the stone is covered, and it ought to take one uniform film of ink and give no sign of difference to show difference of tone. But as a matter of fact it does show a difference, and that difference is probably due to the fact that there is a rubbing process during development, and the less exposed parts come away, leaving the more exposed parts sticking to the stone to different degrees.[10]



(*a*) Before Exposure. Section of Grained Stone Bearing Film of Sensitive Bitumen (Dotted Portion) with a Three-tone Negative
(*b*) The Stone After Exposure and Development. The Difference in the Dotted Portion represents the Difference in the Amount of Bitumen made Insoluble

Figure 1. Bitumen on Grained Stone

Another early writer recognized the same mechanism. He explained:

> The top of each granulation of the stone is covered with only a thin coating of bitumen, which exposure to light, even for a short time or under a comparatively opaque part of the negative, is sufficient to insolubilize right through to the stone. The bottom of each cavity is, on the contrary, filled with a comparatively thick sensitive layer, which can be insolubilized through its whole thickness only by a prolonged exposure, or by exposure under a very transparent region of the negative. The thickness of the bitumen being progressively graduated between these two limits, it can easily be seen that to each tone of the negative there will correspond, after properly conducted development, image elements whose form and distribution are governed by the actual grain of the stone, and whose mean diameter approximately translates the value to be represented.[11]

Diazo Compounds on Aluminum

The major reason for the renewed interest in screenless lithography in the 1950's was the introduction of diazo coated aluminum plates. Recognizing the potential of screenless printing, the Rochester Institute of Technology's Research Center in 1967 undertook a study to "discover the mechanism of continuous-tone printing produced by screenless lithography." Their study was limited to the only types of plates available at the time, negative working and positive working diazo coatings on grained aluminum. They eliminated as possible causes of the continuous-tone effect, the grain of the continuous-tone photographic image used to expose the plate and the grain of the ink structure. They concluded that the grain of the aluminum substrate caused a distribution of coating thickness and that this is the prime cause of the continuous-tone effect.

> The evidence leads us to conclude that the printing plate is the source of the continuous-tone effect observed in screenless lithography. A continuous-tone picture exposed onto a sensitized, grained plate results in a plate image in which the tones of the pictures are represented by ink receptive spots varying in area -- darker tones being represented by larger ink receptive spots than lighter tones. These ink receptive spots on the plate print spots

> of ink of corresponding area on the press sheet thereby producing the various tones in the reproduction. The ability of the plate to produce ink receptive spots varying in area is due to the point-by-point sensitivity distribution across the surface of the plate. This sensitivity distribution is in turn due to the coating thickness distribution formed by the peaks and valleys topography of the grained aluminum plate.[12]

F. Uhlig in a paper presented in 1969 agrees that screenless printing from diazo coated plates requires a variation in the thickness of the light sensitive layer but he determined that it is not necessary for the thickness variation to be the result of substrate graining. He states that the light sensitive layer may be made to vary in thickness or to vary in light sensitivity by several methods. These methods yield softer gradations apparently because they produce a more uniform and symetrical variation in the coating thickness than that produced by random graining of the aluminum. Several novel methods are suggested for producing this type of plate:

> A layer of this structure may be obtained, for instance, by the addition to the coating solution of globules of about 5 microns diameter of a water soluble substance, such as polyvinyl alcohol or gelatin. After drying, the globules are removed by dissolution in water. Alternatively, the light sensitive layer may be embossed with an appropriate mold of glass or steel pins while it is still plastic. In both cases, the desired structure of the layer is produced. . . tiny glass balls may be glued into the support by means of a resin and then hydrophilized by vapour deposition of aluminum, whereupon the light sensitive layer is coated onto the aluminized balls. . . The light sensitive layer may be modified by incorporation of several substances of differing light sensitivity, or by forming pores in the light-sensitive layer by the inclusion of drops of condensed water during coating. Finally, additional layers may be coated on top of the light sensitive layer, or exposure may be effected under light diffusing films, or the light-sensitive layer may be subjected to an additional flash exposure. . .[13]

It can be seen that the mechanism of image formation is the same in both lithographic stones sensitized with bitumen and aluminum sensitized with diazo compounds. This is perhaps not unexpected since both are two-phase plates. That is, the ink receptive image areas are provided by one material, such as the oleophilic bitumen, and the water receptive, non-image areas are provided by a different material, such as the hydrophilic limestone.

The Mechanism of Image Formation In Single-Phase Plates

Bichromated Gelatin Collotype Plates

Technical literature on the collotype process is very limited. Although many articles have appeared in various books and periodicals over the years, they usually give only a superficial description of the process. Some of the early writings on collotype give pages of detailed descriptions of the procedures and formulae, but few scientific explanations.

Of the technical literature available on the process, perhaps the best is that by P. C. Smethurst.[14] Smethurst describes in some detail the fundamental mechanism of image formation in the collotype process as used for facsimile reproductions. He describes this mechanism in terms of the physical behavior of the gelatin matrix. He contends that traditional collotype depends on the formation of a crepe-like grain in the layer of sensitized gelatin. This formation is known as reticulation and by means of reticulation a two-tone image structure is created. This structure consists of a network of constant density lines of varying widths, depending on their exposure, which produce the illusion of continuous tones. Thus the connection between exposure and printed density is essentially an indirect one: "the purpose of light and dichromate is to cause varied intensity of reticulation in the matrix layer when the latter is washed out, and this varied reticulation intensity produces the different tones of the printed image."[15]

It is only when the image structure of a collotype plate has this two-tone quality, says Smethurst, that stability in continuous running can be achieved. While Smethurst feels that reticulation is the fundamental mechanism of image formation in collotype, he says that there is a slight secondary effect which produces some actual, short range, tone gradation in the wider lines.

Charles W. Gamble also describes the grain or reticulation of finished collotype plates and observes that while its general character is the same from plate to plate, it is more pronounced in some than in others. He further states that many collotype plates show so little reticulation "that it may be said to be practically absent, and in this case the differential effect in printing appears to be due to the difference in water absorption alone." Gamble further observes, during a discourse on the causes of reticulation in gelatin layers, that "Ease of printing demands the formation of a well-defined reticulation, though its absence does not mean the plate cannot be printed from - far from it; nor does this mean the grain must be coarse."[16]

Smethurst and Gamble seem to agree that both continuous-tone and two-tone collotype are possible with two-tone collotype accepting the widest range of exposures and giving the most consistent results.

Association Products Plate

Very little research has been done into the mechanism of image formation in the Association Products plate. Although the materials used in this type of plate are in many ways quite different from those used in collotype plates, there is a similarity in performance, and a similarity in the reaction to variables. It may be that the mechanism of image formation is also similar.

Dr. J. L. Silver in one of his patents on the Association Products plate theorizes the mechanism as follows:

> It appears that the image is formed due to the fact that each infinitesimal area of the coating hardens in proportion to the amount of light it receives and consequently becomes less hydrophilic. As in collotype printing plates, the various parts of exposed coating accept water in an amount inversely proportional to the quantity of light they receive. These areas accept a complementary quantity of ink directly proportional to the intensity of light which acted upon the coating. Those areas which receive no light absorb a maximum quantity of water during printing and completely repel the greasy ink. Those areas exposed to sufficient light to render them completely hydrophobic absorb the maximum amount of ink, and those areas which during exposure received intermediate amounts of light accept an intermediate amount of ink in proportion to the intensity of light they received. This apparent mechanism of acceptance and rejection of water and ink proportional to light exposure provides the continuous-tone nature of the printing plate image and the subsequent reproductions.[17]

The interaction mechanism which causes the hydrophilicity of the plate to decrease with exposure is postulated by Dr. Silver in an earlier patent as follows:

> The "association" of the A-stage resin component and the poly-(ethylene oxide) component causes the formation of a tough, hydrophilic material when coated on a substrate or molded. The water receptivity of this "association" product declines as the resole phenolic resin "advances", that is, increases in molecular weight and/or in degree of crosslinking on exposure to light. Radicals released by the action of light on the photosensitive substance in the composition . . . react with the resole phenolic resin to pro-

> duce intermediate chemical products. These products presumably react with each other as well as with unactivated phenolic molecules to produce "advanced" high molecular weight phenolic derivatives. This causes the water receptivity of the A-stage resin-poly (ethylene oxide) coating to decline in proportion to the radicals produced, which is in turn proportional to the intensity of the light received by a particular portion of the coating during exposure.[18]

The question arises, when various parts of the coating accept water in an amount inversely proportional to the quantity of light they receive, what form do these varying amounts of water assume on the plate? Are they films of water of varying thicknesses or are they very fine droplets of water of varying sizes? Further, when these varying amounts of water cause various areas of the plate to accept varying amounts of ink, do these areas also transfer varying amounts of ink to the paper? If so, in what form are the varying amounts of ink transferred? As a random, discontinuous pattern of inked spots with varying areas or as an ink layer of varying thickness? If it is as a pattern of inked spots of varying area, is this caused by the fine droplets of water of varying sizes? If it is as a layer of varying thickness, is this transferred from the plate to the paper as a varying thickness, or does the acceptance and rejection of water and ink in porportion to exposure result in an emulsion of water in ink, selectively diluting the ink, which is then transferred as a constant thickness but dries on the paper as a varying thickness?

FOOTNOTES FOR CHAPTER II

[10] Gamble, pp. 242-244.

[11] L. P. Clerc, *Ilford Manual of Process Work*, (London: Ilford, 1936), p. 261.

[12] Irving Pobboravsky and Milton Pearson, "Study of Screenless Lithography," *Technical Association of the Graphic Arts, Proceedings of the Nineteenth Annual Technical Meeting* (1967), pp. 249-262.

[13] F. Uhlig, "Screenless Offset Printing Process Using Presensitized Printing Plates," *The Journal of Photographic Science* 18 (1970): 6.

[14] P. C. Smethurst, "The Technical Background of the Collotype Process," *The Photographic Journal* 92B (July/August 1952): 115-123.

[15] Ibid., p. 117.

[16] Gamble, pp. 212-228.

[17] Julius L. Silver, "Printing Plate Compositions," Canadian Patent 749,895 (1967).

[18] Julius L. Silver and Barry L. Dickinson, "Photosensitive Compositions and Their Use in Photomechanical Printing," British Patent 983,366 (1965).

CHAPTER III

METHODOLOGY AND RESULTS

Plate Preparation and Presswork

Since the Association Products plates necessary for testing the hypothesis are not available commercially, it was necessary to compound the coating solution and prepare the plates in the laboratory. The exact plate parameters such as coating thickness, curing time and temperature, substrate grain characteristics, etc. were not known, but this was not considered critical to the hypothesis testing. Time did not permit optimization of the plate and printing variables, so only rough tests were conducted to determine reasonable parameter levels which were then held constant. While this procedure did not produce images of the maximum overall quality or widest possible density range, the plates were sufficient for experimental purposes.

The plate coating was prepared according to information contained in the patent literature[19] and supplied by Dr. J. L. Silver. The major ingredients are an ethylene oxide polymer known commercially as Polyox[20] resin and a resole or Bakelite[21] type phenolic resin dissolved in N,N-dimethyl formamide and blended in a high speed vortex blender. The resulting solution was coated on the substrate using a plate whirler and standard coating techniques. The substrate used was a dry blast, coarse grained aluminum marketed by Sumner Williams, Incorporated as "ST Aluminum" and normally used for wipe-on diazo plates. Approximately 50 milliliters of coating solution was used to coat each 10 inch by 15 3/8 inch plate. After whirling until dry, the plates were cured in a laboratory oven for 20 minutes at a temperature of 160°C. The plates were sensitized by rinsing with a one-half percent solution of a diazonium salt, p-diazodiethylaniline zinc chloride, dissolved in methanol. Plate exposures were made through a standard test negative for approximately 30 seconds in a Nu-Arc vacuum exposure frame equipped with a pulsed Xenon light source. The test negative contained as the primary test object a stepped, continuous-tone gray scale ranging in transmission density from .04 to 2.42 in 17 steps. Also included for comparison were several halftone tints of various dot areas.

Presswork was done using an ATF Chief 15 press with the normal, standard equipment except for a sleeve type, paper dampener form roller cover. The fountain solution used was a mixture of 1 1/2 ounces 14° Be gum arabic, 6 drops phosphoric acid, 32 ounces isopropyl alcohol and sufficient water to make two gallons.

Hypothesis Testing

In order for the major hypothesis, that varying water-in-ink emulsification is the mechanism of image formation in Association Products plates, to be true, all of the following sub-hypotheses must be true.

1. The effect of ink emulsification on printed density: other factors being constant, the optical density produced by ink printed on paper must vary inversely with the amount of emulsified water in the ink.

2. The effect of exposure to light on water receptivity: the water receptivity (hydrophilicity) of the Association Products plate must vary

inversely with exposure to light.

3. The water absorbing capability of lithographic ink: the ink used for printing must be capable of being emulsified in the amount necessary (as predicted by sub-hypothesis 1) to produce the optical densities actually obtained.

4. Ink emulsification on the plate: the ink on a given image area of the plate must contain the predicted amount of water necessary to produce the optical density actually printed by that image area.

The methodology used, the results obtained, and the conclusions drawn in testing each of these sub-hypotheses will be discussed separately.

The Effect of Ink Emulsification on Printed Density

A study was undertaken to test the sub-hypothesis that as the amount of emulsified water in an ink increases, the solid ink density on paper printed by that ink decreases. The research question for this study was: Can a set of inks be prepared containing various quantities of emulsified water and with these inks printed samples produced whose optical densities vary with the percent emulsification, and further can this variation be predicted and calculated.

Previous studies

The only located published work in this area seems to dispute the hypothesis. W. H. Banks[22] says his studies have shown that inks containing emulsified water in the range of 10 to 40 percent by volume printed without any substantial reduction in density. A typical set of results from his study is shown in Figure 2. Banks says that the "characteristic low colour intensity" of lithography is not due to water emulsified in the ink but to a surface film of water causing reduced ink transference at each nip and at the blanket to paper transfer. His results purport to show that density does not vary significantly with emulsification. However, notice that in Figure 2 the "arbitrary ink settings" on the abcissa are not defined. Each of these settings will yield a specific yet undefined ink layer thickness on the paper. Notice that with black ink, settings above about no. 6 seem to yield an ink layer thickness sufficient to give maximum density and that the lowest density obtained with unemulsified black is 1.0. Is the machine ink setting of 1 to 10 a typical range for offset lithography? What happens if the ink settings are reduced further so as to yield densities nearing zero?

Emulsification of water in effect dilutes the ink, and other factors being constant it will dry on the paper to a thinner ink layer than less emulsified ink, thus producing a lower density. There is, on the other hand, an ink layer thickness above which there will be little or no further increase in density. This maximum density is called the saturation density. For a given set of process conditions, this density cannot be exceeded regardless of the ink layer thickness. The minimum ink layer thickness which will yield the saturation density might be termed the saturation thickness. So, if inks of various degrees of emulsification are fed at ink fountain settings that will when dry yield the saturation thickness or thicker, relatively constant densities at or near the saturation density will be obtained. One then might draw the erroneous conclusion that density does not vary with emulsification. This was perhaps the case in Banks' study, and if densities are measured at ink layer

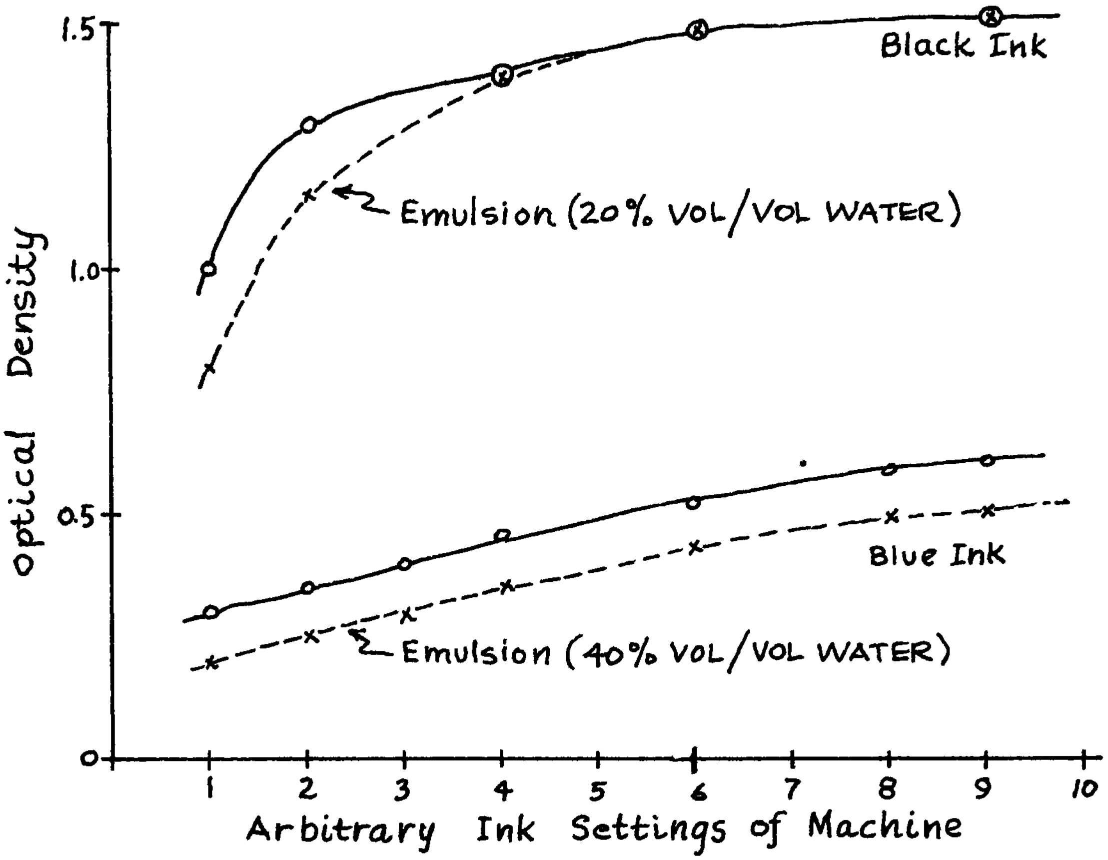


Figure 2. W. H. Banks' Emulsification-Density Curves

thicknesses less than the saturation thickness it will be seen that emulsification will produce decreasing densities.

Methodology and results

Dr. D. Tollenaar, in his paper "Optical Density and Ink Layer Thickness"[2 3], presents an equation for the density versus ink layer thickness curve. This is $D = D_\infty(1-e^{-mx})$ where D is the optical density, D_∞ is the saturation density, that is the maximum density obtained with very thick layers, x is the ink layer thickness in microns and m is the increase of the relative density D/D_∞ per unit increase of ink layer thickness at very thin layers. The values of m and D_∞ can be obtained for a given ink and paper combination by measuring the optical densities produced at two particular ink layer thicknesses. The equations for this are given at the bottom of Table 1. From these values of m and D_∞, the density versus ink layer thickness curve can be plotted.

The values of m and D_∞ were determined for IPI Speed King Litho Ink, Neutral Black (PMS) printed on Mead "Black and White", 70 pound, enamel paper. Specific ink layer thicknesses were printed using the IGT Printability Tester. This is a small, precision, press-like testing device consisting of an inking unit, a printing unit and an ink pipette for accurately measuring small quantities of ink. Substituting in the equation, density values D for layers from 0.1 µm to 8.0 µm in 25 increments were calculated.

If, in fact, the emulsification of a given amount of water in the ink dilutes the ink and results in a proportionally thinner ink layer when dried, then similar density curves can be mathematically calculated from this same data for various percentages of water in the ink. These calculated density curves for various percentages of water in ink are shown in Figure 3 and Figure 4. The data on which these curves are based are given in Table 1.

Actual samples were then printed at various ink layer thicknesses on the IGT Printability Tester using both unemulsified ink and ink emulsified with various percentages of water. The densities of these samples agreed closely with the calculated predicted densities. Comparisons between the measured and calculated densities are shown in Table 2.

Table 1. Calculated Density Versus Layer Thickness by Percent of Emulsified Water

Xw	Percent Water													
	0		20		40		60		80		90		95	
	Xd	D	Xd	D	Xd	D	Xd	D	Xd	D	Xd	D	Xd	D
0.10	0.10	0.16	0.08	0.12	0.06	0.09	0.04	0.06	0.02	0.03	0.01	0.02	--	--
0.20	0.20	0.30	0.16	0.24	0.12	0.18	0.08	0.12	0.04	0.06	0.02	0.03	0.01	0.02
0.30	0.30	0.43	0.24	0.35	0.18	0.27	0.12	0.18	0.06	0.09	0.03	0.05	--	--
0.40	0.40	0.56	0.32	0.46	0.24	0.35	0.16	0.24	0.08	0.12	0.04	0.06	0.02	0.03
0.50	0.50	0.68	0.40	0.56	0.30	0.43	0.20	0.30	0.10	0.16	0.05	0.08	--	--
0.60	0.60	0.79	0.48	0.66	0.36	0.51	0.24	0.35	0.12	0.18	0.06	0.09	0.03	0.05
0.70	0.70	0.89	0.56	0.75	0.42	0.58	0.28	0.41	0.14	0.21	0.07	0.11	--	--
0.80	0.80	0.99	0.64	0.83	0.48	0.66	0.32	0.46	0.16	0.24	0.08	0.12	0.04	0.06
0.90	0.90	1.08	0.72	0.91	0.54	0.72	0.36	0.51	0.18	0.27	0.09	0.14	--	--
1.00	1.00	1.16	0.80	0.99	0.60	0.79	0.40	0.56	0.20	0.30	0.10	0.16	0.05	0.08
1.25	1.25	1.35	1.00	1.16	0.75	0.94	0.50	0.68	0.25	0.37	0.12	0.18	0.06	0.10
1.50	1.50	1.51	1.20	1.32	0.90	1.08	0.60	0.79	0.30	0.43	0.15	0.23	0.08	0.12
2.00	2.00	1.76	1.60	1.57	1.20	1.32	0.80	0.99	0.40	0.56	0.20	0.30	0.10	0.16
2.50	2.50	1.94	2.00	1.76	1.50	1.51	1.00	1.16	0.50	0.68	0.25	0.37	0.12	0.19
3.00	3.00	2.06	2.40	1.91	1.80	1.67	1.20	1.32	0.60	0.79	0.30	0.43	0.15	0.23
3.50	3.50	2.16	2.80	2.02	2.10	1.80	1.40	1.45	0.70	0.89	0.35	0.50	0.18	0.26
4.00	4.00	2.22	3.20	2.10	2.40	1.91	1.60	1.57	0.80	0.99	0.40	0.56	0.20	0.30
4.50	4.50	2.27	3.60	2.16	2.70	1.99	1.80	1.67	0.90	1.08	0.45	0.62	0.22	0.33
5.00	5.00	2.30	4.00	2.22	3.00	2.06	2.00	1.76	1.00	1.16	0.50	0.68	0.25	0.37
5.50	5.50	2.32	4.40	2.26	3.30	2.12	2.20	1.84	1.10	1.24	0.55	0.74	0.28	0.40
6.00	6.00	2.34	4.80	2.29	3.60	2.17	2.40	1.91	1.20	1.32	0.60	0.79	0.30	0.43
6.50	6.50	2.35	5.20	2.31	3.90	2.21	2.60	1.97	1.30	1.39	0.65	0.84	0.32	0.47
7.00	7.00	2.36	5.60	2.33	4.20	2.24	2.80	2.02	1.40	1.45	0.70	0.89	0.35	0.50
7.50	7.50	2.37	6.00	2.34	4.50	2.27	3.00	2.06	1.50	1.51	0.75	0.94	0.38	0.53
8.00	8.00	2.37	6.40	2.35	4.80	2.29	3.20	2.10	1.60	1.57	0.80	0.99	0.40	0.56

Xw = wet layer thickness of emulsified ink in micrometers
Xd = dried layer thickness of emulsified ink in micrometers
D = optical density

$X_1 = 2\mu,\ D_1 = 1.76 \quad X_2 = 4\mu,\ D_2 = 2.22$

$$M = -\frac{1}{X}\ln\left(\frac{D_2}{D_1} - 1\right) = -\frac{1}{2}\ln\left(\frac{2.22}{1.76} - 1\right) = 0.671$$

$$D\infty = \frac{D_1}{1-e^{-mx_1}} = \frac{1.76}{1-e^{-(.671)(2)}} = 2.38$$

$$D = D\infty(1-e^{-mx}) = 2.38\ (1-e^{-0.671x})$$

Table 2. Measured Density Versus Ink Layer Thickness by Percent of Emulsified Water

% Water in Ink	Vol. of Ink-Water in cc.	Vol. of ink in cc.	Calculated Ink Layer (µm)		Measured Optical Density				Calc. Density
			Wet	Dry	Pnt.1	Pnt.2	Pnt.3	Avg.	
0.0	1.000	1.000	8.00	8.00	2.44	2.43	2.48	2.45	2.37
0.0	0.500	0.500	4.00	4.00	2.21	2.24	2.22	2.22	2.22
0.0	0.250	0.250	2.00	2.00	1.78	1.76	1.74	1.76	1.76
0.0	0.125	0.125	1.00	1.00	1.21	1.16	1.14	1.17	1.16
13.4	1.000	0.866	8.00	6.93	2.40	2.40	2.42	2.40	2.36
13.4	0.500	0.433	4.00	3.46	2.16	2.22	2.20	2.19	2.15
13.4	0.250	0.217	2.00	1.74	1.68	1.69	1.66	1.68	1.64
13.4	0.125	0.108	1.00	0.86	1.09	1.07	1.04	1.07	1.04
22.0	1.000	0.780	8.00	6.24	2.46	2.44	2.36	2.42	2.34
22.0	0.500	0.390	4.00	3.12	2.15	2.16	2.12	2.14	2.09
22.0	0.250	0.195	2.00	1.56	1.64	1.63	1.59	1.62	1.55
22.0	0.125	0.098	1.00	0.78	1.10	1.08	1.06	1.08	0.97
32.1	1.000	0.679	8.00	5.43	2.26	2.32	2.26	2.28	2.32
32.1	0.500	0.340	4.00	2.72	2.00	1.98	2.00	1.99	2.00
32.1	0.250	0.170	2.00	1.36	1.42	1.42	1.37	1.40	1.43
32.1	0.125	0.085	1.00	0.68	0.90	0.85	0.77	0.84	0.87

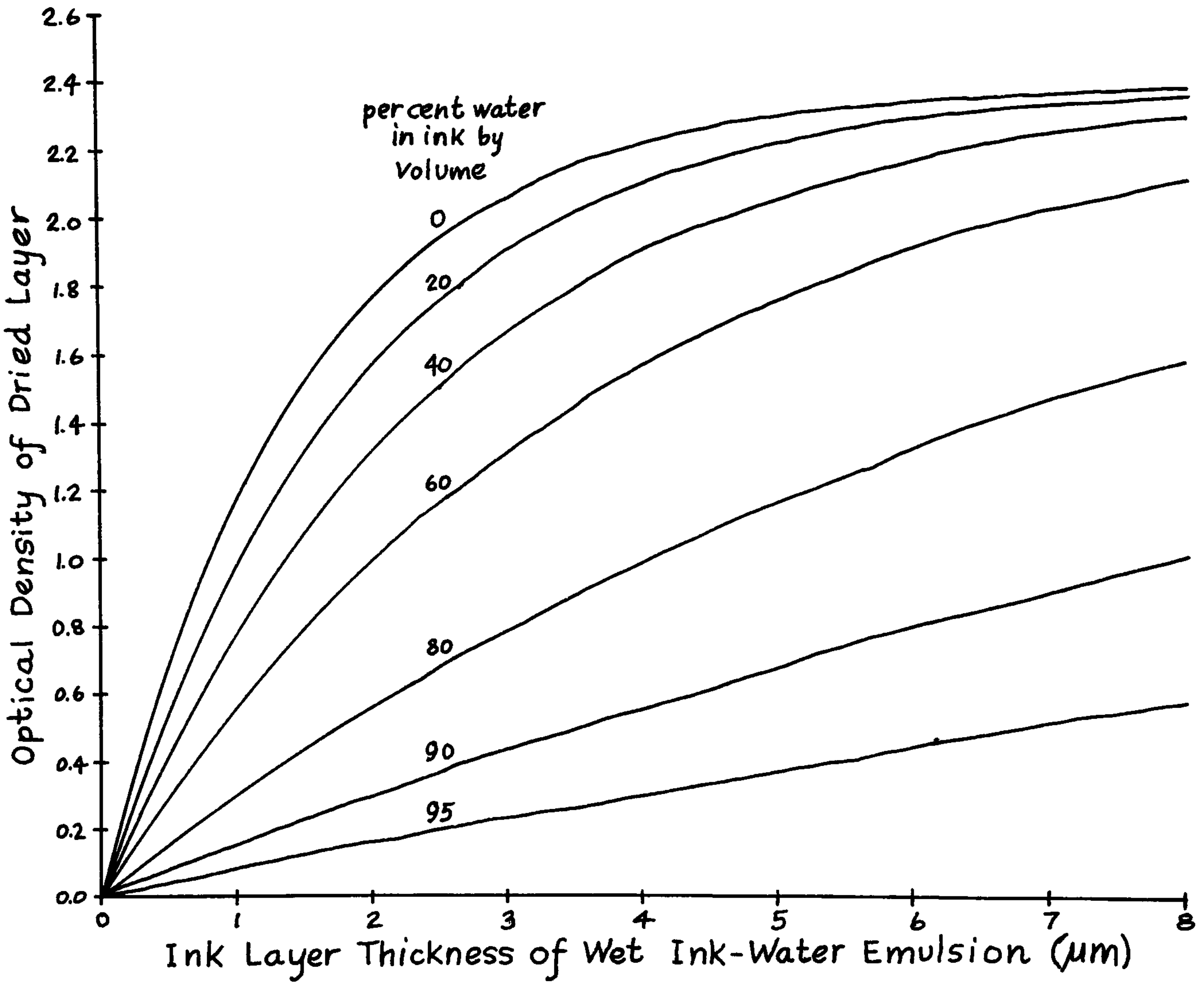


Figure 3. Layer Thickness Versus Density

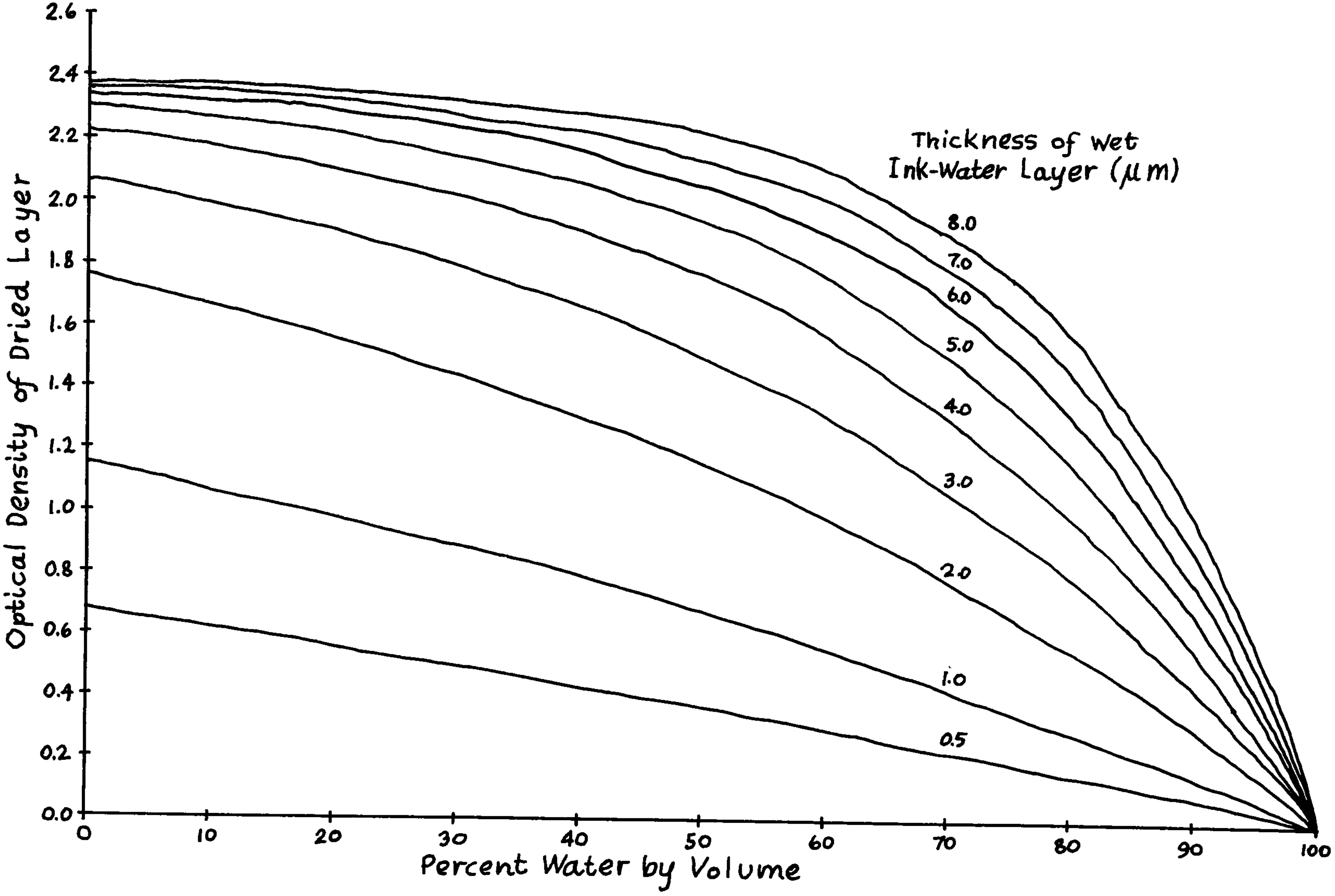


Figure 4. Emulsification Versus Density

Conclusions

The optical density of ink on paper varies inversely with the percent of emulsified water and directly with the ink layer thickness. The relationships between density, percent emulsification, and layer thickness for a given ink and paper combination can be accurately predicted using the IGT Printability Tester and the method described. The particular ink and paper combination used in this study is reasonably typical. The results show that at ink layer thicknesses normally encountered in offset lithography, about one to three microns, the effects of emulsification on printed density are significant.

The Effect of Exposure to Light on Water Receptivity

Contact angles

In order to quantitatively determine the water receptivity of the Association Products plate and its variability with exposure, a measurement called the contact angle was used. The contact angle is frequently used in lithographic research as a measurement of the attraction of a liquid for a solid surface. Referring to Figure 5, the contact angle is defined as the angle θ formed by the surface and a line drawn tangent to the liquid drop at its intersection with the surface. If, for example, a drop of water were placed on a metal surface such as a printing plate, the drop would spread depending on the relative attraction of the water for the surface of the metal and for itself. At the extreme of total wettability (total water receptivity), the drop would spread to cover the entire surface and would have a contact angle of 0°. At the other extreme

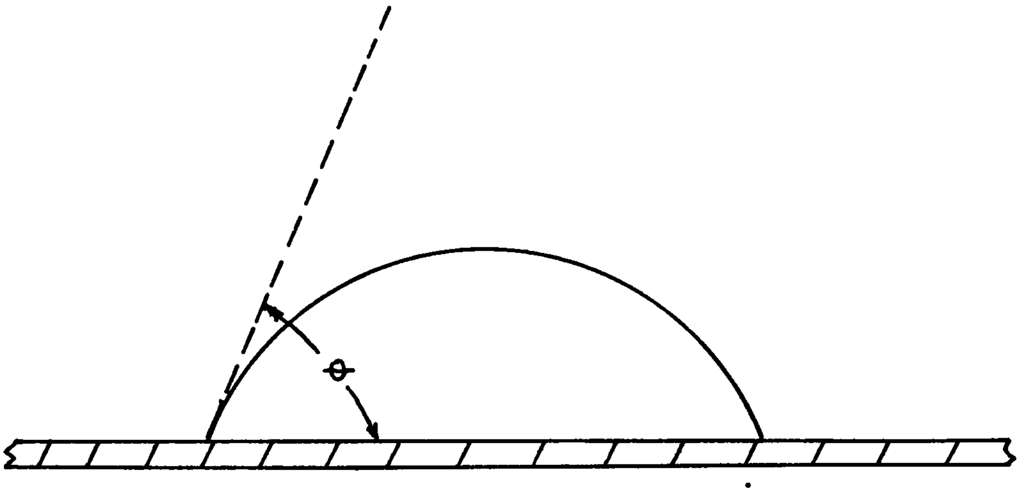


Figure 5. Contact Angle

of total non-wettability, the drop would not spread at all and would have a contact angle of 180°. In practice, such extreme angles are not normally encountered.

In standard lithographic plates, such as might be used for the halftone process, it is desired to obtain the maximum difference between the ink receptivity of the image and non-image areas. Therefore the image or ink receptive areas of such plates would have a water contact angle approaching 180°, and the non-image or ink repellent areas would have a water contact angle approaching 0°.[24]

Methodology and results

If, in fact, the Association Products plate prints continuous tones by emulsifying the ink to varying degrees, then it must be true that the plate attracts and holds varying quantities of water to various areas of the image depending on the exposure to light that area has received. In order to test this, a plate was exposed through a stepped, continuous-tone gray scale. The transmission density of the steps varied in approximately 0.15 increments with a total range of from 0.14 to 2.42. Each density increase of 0.30 on the gray scale reduces the net exposure by one-half. After normal processing and drying of the plate, a drop of water was carefully placed in turn on each step of the gray scale. An enlarged silhouette of the drop was projected onto a screen by use of a light source and lens arrangement. The width and height of the drops as projected were measured. From these two measurements the contact angle was determined using the formula derived in Figure 6.

Table 3 lists the results obtained from these measurements, and Figure 7 is a graph of the contact angle versus exposure.

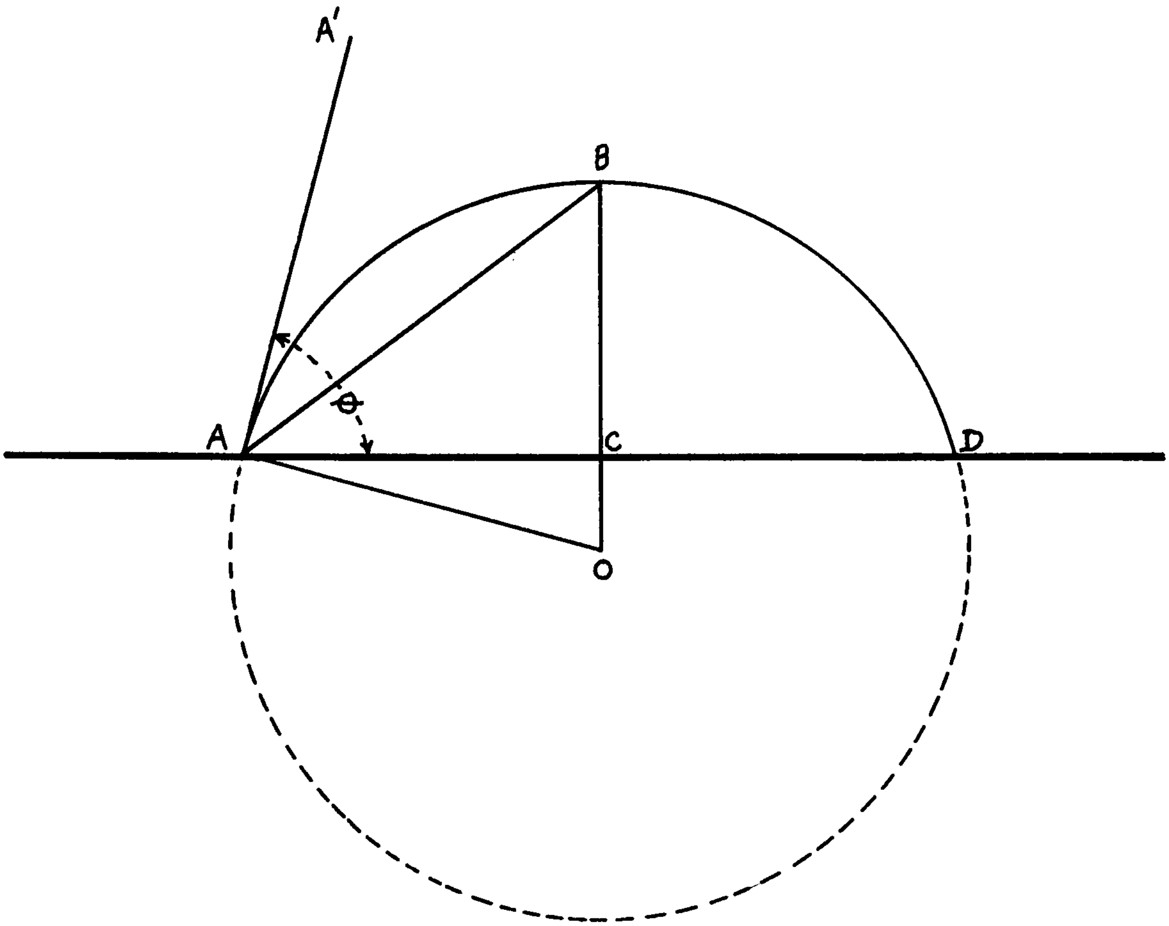
Conclusions

The results show that with no exposure the plate is very water receptive as indicated by the low contact angle. With increasing exposure the contact angle increases indicating a decreasing water receptivity. This ability of the plate to attract and hold varying amounts of water in various portions of the plate was also readily observed by lightly wiping the surface of the plate with a moistened cotton pad.

It is concluded that the water receptivity (hydrophilicity) of the Association Products plate varies inversely with exposure to light.

The Water Absorbing Capability of Lithographic Ink

Referring to Figure 3 on page 31, it can be seen that in order for the range of tones (optical densities) which are actually produced by the Association Products plate to be due to emulsification, it is necessary for the ink to absorb up to approximtely 95 percent water. A test of emulsification as the image mechanism was performed by measuring the water absorbing capability of a group of lithographic inks and by printing from



Arc ABD is the profile of the projected water drop. Line AA' is drawn tangent at Point A. Angle A'AC is defined as the contact angle θ.

Given distances AD and BC, determine θ.

OA = OB both being radii of the circle, and therefore ∠OAB = ∠OBA being angles of a triangle subtended by equal sides.

∠OAA' = 90° being constructed tangent, therefore ∠OAC = $90^{\circ}-\theta$.

Since ∠OCA = 90°, ∠AOC = θ by subtraction from 180°.

$\theta = 180^{\circ} - 2\angle OBA$, $\tan \angle OBA = \frac{AC}{BC}$, $\angle OBA = \arctan \frac{AC}{BC}$, $AC = \frac{AD}{2}$

therefore $\theta = 180^{\circ} - 2 \arctan \frac{AD}{2BC}$

Figure 6. Contact Angle Calculation

Table 3. Contact Angle Measurements

Sens. Guide Step	Density	% Trans.	Contact Angle in Degrees							
			Replicate Number						Std. Dev.	Mean
			1	2	3	4	5	6		
1	0.04	91.2	64.9	67.4	52.3	50.2	63.9	78.8	10.5	62.9
2	0.19	64.6	64.0	57.0	49.9	43.6	63.8	79.4	12.5	59.6
3	0.35	44.7	62.3	59.3	44.7	49.3	63.7	75.3	10.9	59.1
4	0.50	31.6	57.2	54.8	42.0	49.1	58.0	64.7	7.9	54.3
5	0.65	22.4	48.9	54.1	45.3	48.5	48.6	54.7	3.6	50.0
6	0.78	16.6	52.0	49.9	49.2	46.1	41.2	47.7	3.8	47.7
7	0.93	11.8	47.2	49.0	43.1	47.1	34.2	42.2	5.4	43.8
8	1.09	8.1	40.6	45.8	45.4	46.4	32.7	43.9	5.2	42.5
9	1.23	5.9	44.3	41.7	46.6	45.9	34.0	41.5	4.6	42.3
10	1.36	4.4	30.8	45.5	50.4	42.3	31.8	41.0	7.7	40.3
11	1.50	3.2	37.9	37.6	38.4	39.7	30.6	38.3	3.3	37.1
12	1.64	2.3	32.3	34.0	32.1	34.8	31.6	39.4	2.9	34.0
13	1.82	1.5	30.4	39.3	35.5	34.7	29.3	40.9	4.6	35.0
14	1.97	1.1	39.7	34.4	33.6	31.0	26.7	37.6	4.6	33.8
15	2.12	0.8	33.7	41.4	26.8	29.5	29.3	39.2	5.9	33.3
16	2.26	0.5	43.6	45.8	30.3	31.1	--	--	8.1	37.7
17	2.42	0.4	36.5	46.1	28.1	29.0	--	--	8.3	34.9
no exp.	--	0.0	29.4	35.3	27.4	25.8	29.7	33.8	3.7	30.2

NOTE: Overall exposure time was 20 seconds. Individual net exposures may be calculated from percent transmission.

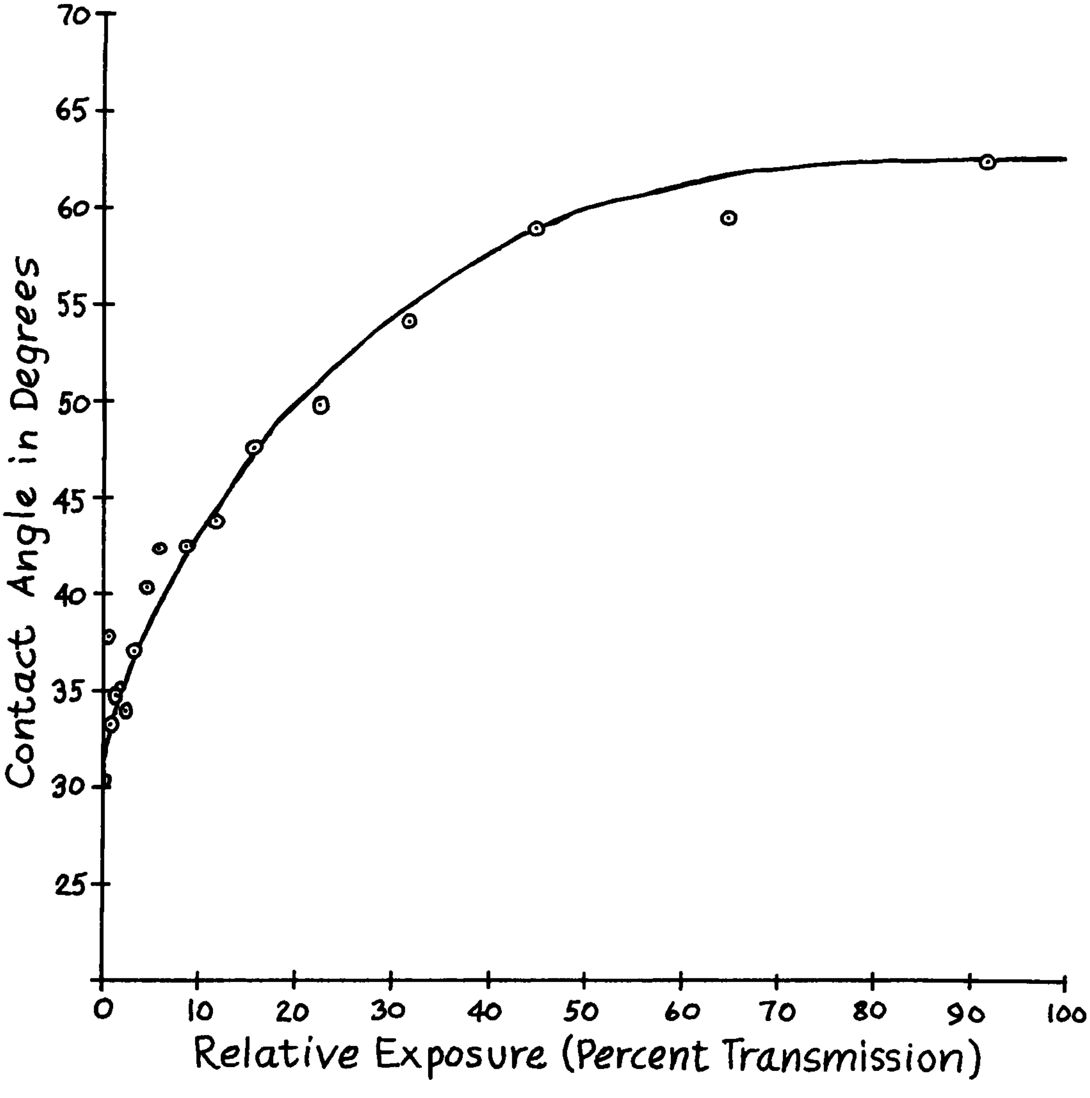


Figure 7. Contact Angle Versus Exposure

an ink highly resistant to emulsification and from an ink highly prone to emulsification.

Water absorption test

A group of five lithographic inks were obtained which the manufacturer felt represented a typical range of water absorption capability. The water absorption capability of these inks was tested using a procedure similar to the lithographic ink breakdown test formulated by the New York Printing Ink Production Club.[25] Approximately ten grams of ink and 50 cc. of water were mixed for a period of five minutes, at which time the supernatant water was poured off. The ink was weighed before and after mixing to determine the amount of water absorbed. This test proved to be reasonably repeatable. The inks tested ranged from 12 to 32 percent water absorption by volume as shown in Table 4. The two inks at the extremes of the range were then used for printing from the same Association Products plate. The image consisted of the stepped, continuous-tone gray scale previously described plus a group of halftone tints ranging from 20 percent to 90 percent dot area.

Conclusions

No significant difference was observed between the images produced by the two inks. If emulsification is the image forming mechanism, a marked difference should be observed in the densities produced by the two inks as indicated by the gray scale steps reproduced; while no difference should be observed in the number of halftone tints reproduced. If the water absorption test correlates with actual emulsification conditions on the plate during printing, it can be seen from Figure 3 and Figure 4 that at a wet ink layer thickness of 1.5 μm the lowest optical density that should be printed with an ink emulsifying up to 12.0 percent is 1.40. With an ink emulsifying up to 32.2 percent, the lowest density printed should be 1.18. The actual lowest optical density printed from each ink was 0.15.

It is concluded that the ink used for printing is not capable of being emulsified in the amount predicted as necessary by sub-hypothesis 1, to produce the optical densities actually obtained.

Table 4. Water Absorption Test

Type of Ink	Percent Water by Wgt.				Percent Water by Vol.			
	Replicate No.			Avg.	Replicate No.			Avg.
	1	2	3		1	2	3	
Ronico XL-93202	13.0	9.9	11.5	11.5	13.6	10.3	12.0	12.0
Ronico A-3410	21.2	21.0	17.6	19.9	22.0	21.8	18.3	20.7
Ronico A-2785	24.8	24.1	22.8	23.9	25.7	25.0	23.6	24.8
IPI Speed King	27.0	36.3	30.0	31.1	28.0	37.5	31.0	32.2

Ink Emulsification on the Plate

Figure 4 on page 32 shows for various ink layer thicknesses the percent of emulsified water that must be present in a given image area of the plate in order to produce a particular printed density. As a final test of the hypothesis of emulsification as the mechanism of image formation, measurements were made of the percent of water in a particular image area of the plate and of the printed density produced by this area. If the hypothesis is valid, these measurements should agree with the predicted values.

Determination of water content by infra-red analysis

One method frequently employed for determing the water content of lithographic inks is evaporation at elevated temperatures with an allowance being made for any non-aqueous volatile materials. Another method sometimes used is titration with Karl Fisher reagent. Each of these methods, however, requires a sample of at least several grams. Because it is not possible to collect such large samples from the printing plate, a method for evaluating very small samples was required.

A method for the determination of the water content of lithographic printing inks by infra-red analysis was described by Cartwright and Harden:

> The infra-red absorption spectra of lithographic printing inks generally show two well marked peaks at frequences of 3500 cm^{-1} and 1740 cm^{-1} corresponding respectively to hydroxyl and carbonyl groups. When measurements are made with a suitable spectrophotometer the absorbance at these wavelengths will vary according to the thickness of the sample measured, but the ratio of absorbance of hydroxyl group/ absorbance of carbonyl group (D_{OH}/D_{CO}) will remain approximately constant for a given ink. If water is now added to the ink the hydroxyl peak is increased while the carbonyl peak remains unchanged. Thus the addition of water will increase the ratio D_{OH}/D_{CO}. If calibration curves are prepared in which graphs are plotted of D_{OH}/D_{CO} against known content of added water, the water content of an unknown sample can be determined once the D_{OH}/D_{CO} ratio is known.[26]

This method proved ideal for the purpose as only an extremely small sample of ink is necessary.

The infra-red analyses were conducted by measuring ink samples between rock salt plates using a Perkin Elmer Model 257 Spectrophotometer. Measurements of infra-red absorption were made between 4000 cm^{-1} and 625 cm^{-1} (2.5 μm to 16 μm). A typical spectrophotometer recording trace is shown in Figure 8. The percent transmittance for the hydroxyl group peak and the carbonyl group peak respectively was measured from the base lines drawn as indicated. Since the transmittance (T) of the groups is not proportional to the concentration, it is necesary to convert these readings to absorbance (D). Absorbance is proportional to the group concentration and is equal to -log T.

Results

Samples of IPI Speed King Litho Ink, Neutral Black (PMS), were used to prepare the required calibration curve. One sample was ink as received from the supplier which was assumed to contain no water. Two additional samples were prepared by emulsifying a known amount of water into the ink to produce mixtures containing 11.2 and 29.6 percent water by volume respectively. Small portions from these samples were placed between rock salt plates for the infra-red analysis. A small quantity of Nujol was used to assist in spreading the ink. Several measurements were made from each sample. The resulting calibration chart is shown in Figure 9.

Ink samples were collected from three Association Products plates immediately after these plates had printed images using the IPI ink and Mead Enamel paper. The optical densities of the images produced by the selected sample areas were measured and the plate ink samples were analyzed for water content. The results are shown in Table 5. Also shown is the predicted amount of emulsified water necessary to produce these measured optical densities. These values are as predicted by the density-percent water curves of Figure 4. The appropriate ink layer thickness curve for each sample was determined by measuring the optical density of a maximum exposure, solidly inked patch on the printed sheet.

Table 5. Water Measurements on the Plate

Sample No.	Solid Ink Density	Ink Layer Thickness	Sample Area Density	Predicted Percent Water	D_{OH}/D_{CO}	Measured Percent Water
1	1.87	2.3 μm	1.62	26	0.44	4
2	1.59	1.6 μm	1.03	49	2.05	23
3	1.44	1.4 μm	0.95	46	2.01	22

Conclusions

As can be seen from Table 5, the amounts of water actually present in the ink on the plate are significantly different from the predicted amounts. It should be remembered that in collecting ink samples from the plate it is not possible to distinguish between surface water and emulsified water, so to the extent that surface water was present in the areas sampled the water percentages are high. Even considering this source of error, the measured water percentages are consistently and significantly lower than the predicted values.

It is concluded that the ink on a given image area of the plate does not contain the predicted amount of water necessary to produce the optical density actually printed by that image area.

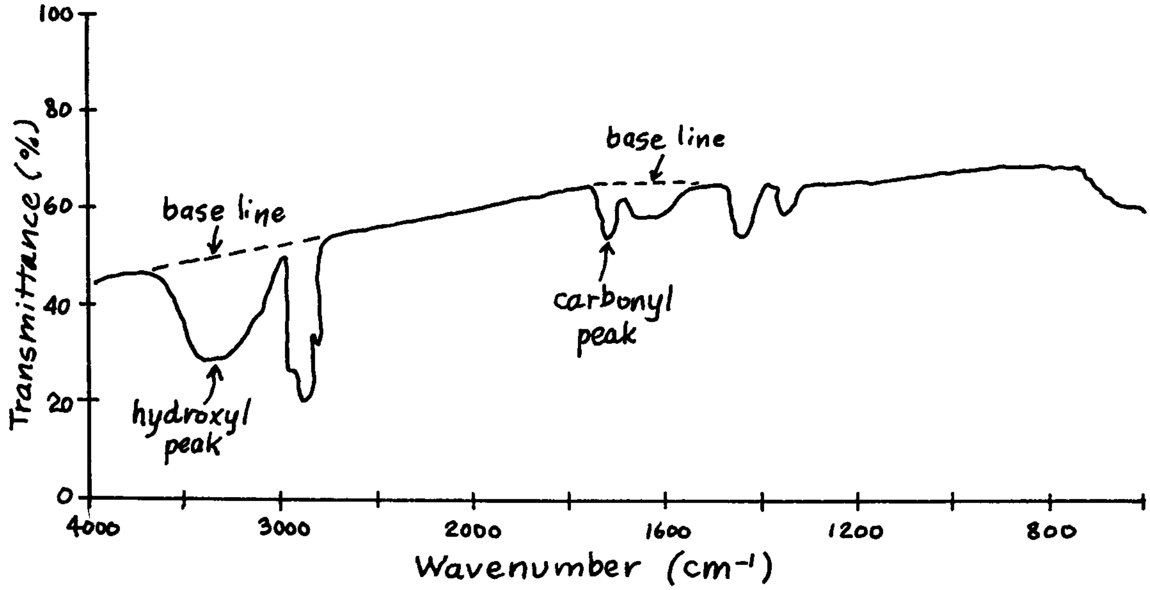


Figure 8. Typical Spectrophotometer Recording Trace

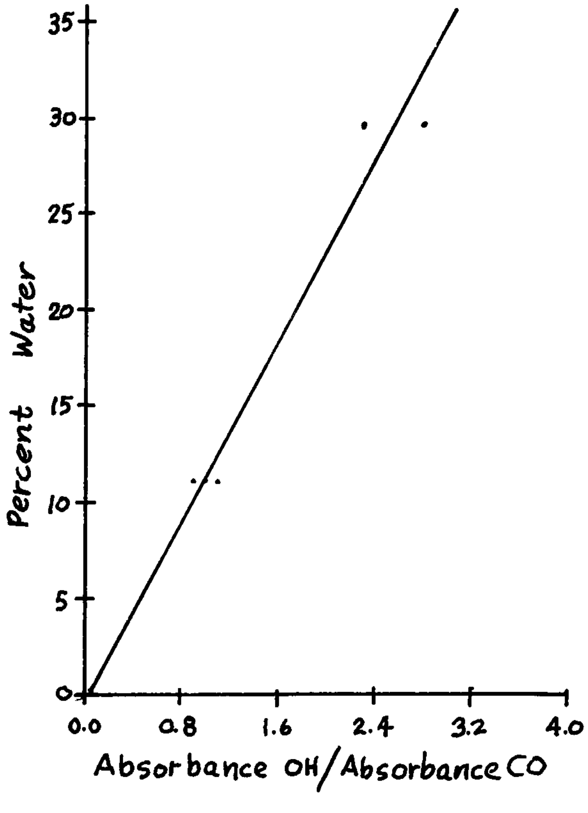


Figure 9. Calibration Chart

FOOTNOTES FOR CHAPTER III

[19] J. L. Silver and B. L. Dickinson, "Photosensitive Compositions and Their Use in Photomechanical Printing," British Patent 983,366 (1965); U. S. Patents 3,231,377 (1966) and 3,231,381 (1966).

J. L. Silver, "Printing Plate Compositions," Canadian Patent 749,895 (1967) and U. S. Patent 3,309,202 (1967).

J. L. Silver, "Positive Planographic Printing Plates," U. S. Patent 3,514,288 (1970).

[20] Polyox is a registered trademark of Union Carbide Co. and designates a number of their poly(ethylene oxide) resins of varying molecular weight ranges.

[21] Bakelite is a registered trademark of Union Carbide Co.

[22] W. H. Banks, "Some Phenomena Affecting Print Quality," The British Ink Maker (August 1965): 198.

[23] D. Tollenaar and P. A. H. Ernst, "Optical Density and Ink Layer Thickness," Advances in Printing Science and Technology, vol. 2 (Oxford: Pergammon Press, 1962), pp. 214-233.

[24] R. A. C. Adams, "Contact Angles and Their Signifcance in Lithographic Research," International Bulletin for the Graphic Arts (January 1956): 20.

[25] R. F. Bowles and W. F. Reich, "An Emulsification Test," The British Ink Maker (February 1959): 38.

[26] P. F. S. Cartwright and G. D. Harden, "Determination of the Water Content of Lithographic Printing Inks by Infra-Red Analysis," The British Ink Maker 7 (February 1965): 86.

CHAPTER IV

SUMMARY AND CONCLUSIONS

Of the four sub-hypotheses discussed in the preceeding chapter, the one dealing with the effect of ink emulsification on printed density is unquestionably the most important. Based on Tollenaar's equation, mathematical relationships were developed relating density, percentage of emulsified water, and ink layer thickness. This provided the foundation for hypothesis testing. These mathematical relationships allowed prediction of the amount of water-in-ink emulsification necessary to produce a given range of optical densities as well as a prediction of the amount of ink emulsification expected on a given plate area associated with a particular printed density.

Testing revealed that neither of these predicted and necessary conditions existed in actual printing from the plates. As was shown, a printed density of approximately 0.15 could be produced from ink capable of only 12 percent emulsification. If emulsification were the image producing mechanism, this could not be done. An ink capable of emulsification in the 90 percent range would be required. Further, a plate image area producing a 0.95 printed density would be expected to contain 46 percent water emulsified in the ink, but this was not the case. Such ink contained only 22 percent water.

These facts force us to conclude that the hypothesis is invalid. The continuous-tone image of the Association Products plate is not produced by selective emulsification of the ink. This is not to say that emulsification has no effect at all, but only that it is not the mechanism of image formation.

It has been said that even in proving an hypothesis invalid, valuable information can still be obtained. One of the ways that this might be true in this case is that emulsification may well have effects in halftone printing not previously considered. For example, it has been suspected by a number of researchers that ink layer thickness varies with dot size, particularly in very small dots.[27] Yule and Neilsen state that "It is not certain that the small dots carry as heavy a layer of ink as the solid."[28] Emulsification might be the reason for this apparent varying layer thickness. It is conceivable that some amount of selective emulsification takes place, particularly in areas with very small dots. This could be due to the higher ratio of non-image area surface water to ink. As we have shown, this would result in a thinner ink layer thickness once this emulsified ink dried on the paper. Previously, emulsification was not normally expected to affect ink layer thickness or density and was therefore not considered as a variable in the relationship between dot size and density.

FOOTNOTES FOR CHAPTER IV

[27] Richard J. Byer, "Ink Film Thickness and Its Relation to Dot Size in Photo Offset Lithography," (Report for the Department of Photographic Science, Rochester Institute of Technology, May 1969), p. 1.

[28] J. A. C. Yule and W. J. Neilsen, "The Penetration of Light Into Paper and Its Effect on Halftone Reproduction," *Technical Association of the Graphic Arts*, *Proceedings of the Third Annual Technical Meeting* (1951), pp. 65-76.

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