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THE EFFECT OF SILICIC ACID IN THE FOUNTAIN SOLUTION

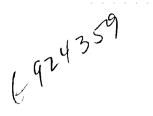
ΒY

Kayode S. Ajibade

A thesis submitted in partial fulfillment of the requirements 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

May, 1977

Thesis advisor: Dr. Julius L. Silver



School of Printing Rochester Institute of Technology Rochester, New York

CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's Thesis of

Kayode S. Ajibade

With a major in Printing Technology has been approved by the Thesis Committee as satisfactory for the thesis requirement for the Master of Science degree at the convocation of

May, 1977

Thesis Committee:

Thesis adviser

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THE EFFECT OF SILICIC ACID IN THE FOUNTAIN SOLUTION

by Kayode S. Ajibade

An Abstract

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My appreciation is also extended to my mother, Adekunraju, and my brother, Abioye Ajibade, for their encouragement. Silicic acid is a water soluble colloidal resin which can be obtained commercially. The effect of silicic acid as a desensitizer in fountain solution was studied. The resin of this colloidal solution was compared to gum arabic solution.

The study included the investigation of the physical properties of the solution at different concentrations as well as press performance. Comparisons were drawn regarding wettability, viscosity, surface tension, dot size change, minimum dampening rate to clean-up the non-image areas, resolution, resistance to scum, blinding of image areas, rate of de-inking over-run non-image areas, performance distinction between lithium silicate and sodium silicate, and changes with aging in solubility properties of silicates in fountain solutions.

The experiments were carried out under carefully controlled conditions; the only variable present was one ingredient of the fountain solution. The concentration of the necessary solution was determined. The effect of concentration was discussed and reported. A considerable number of the results were statistically analyzed by the two factor analysis of variance.

The effectiveness of silicic acid solution as a substitute for gum arabic solution varied. Silicic acid is comparable in regard to the ability of the solution to clean the plate with minimum number of sheets, resistance to scum, resolution, and blinding of image areas. Performance distinctions between lithium silicate and sodium silicate and solubility properties of silicates with aging were noted.

Gum arabic produces smaller changes in dot size and does not blind images as quickly as silicic acid does. The advantages of silicic acid are good resistance to bacterial attack, longer shelf life, and better wetting of the plate than gum arabic when properly diluted.

Abstract	approved:		thesis advisor		visor
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CHAPTER I

INTRODUCTION

A considerable percentage of offset-litho problems are estimated to be caused by the ink-water relationship.¹ Excess moisture picked up on the plate works its way back into the inking system and the action of the rollers causes emulsification of ink and water. The excess water dilutes the irk and causes lower print densities. Because a lithographic plate is planographic, the separation between non-image and image areas is said to be chemically selective. It is important that the non-image area becomes hydrophilic while the image area maintains hydrophobicity. Substances such as oil and water are composed of molecules which have affinity for each other because of adhesive forces which exist between them.

> "The forces arising between the molecules of one material are called cohesive forces and hold the molecules of a particular substance together to give the form, shape and characteristics to the materials that surround them. There are also forces existing between the molecules of two different materials which are called adhesive forces and these hold the molecules of two different substances together."²

When the cohesive forces of oil/water are greater than their adhesive forces, they do not mix. Lithographic inks have a high cohesion while water has a low cohesion. Because of the low cohesion of water, better wetting is achieved on the plate. Therefore, oil molecules will associate with oil attracting molecules that consist of the image areas of a plate, and water molecules will associate with the water attracting areas. To arrange these components oil attracting and water attracting areas - and balance between adhesive and cohesive forces to achieve the ink and water separation, the plate needs to be desensitized.

In lithographic printing it is necessary to keep the non-image areas moistened with fountain solution so that they will not accept ink. As a result, the quality of the printed product will be predominantly dependent upon the composition, and control of the fountain solution in its application to the surface of the plate. Basically, the fountain solution is composed of:

- 1. A desensitizing gum e.g., gum arabic, cellulose gum or hydrogum (mesquite gum).
- An acid very often phosphoric acid or an acid phosphate salt. Sometimes gallic or tannic acid is used.
- 3. Ammonium bichromate and/or a nitrate salt such as ammonium nitrate, zinc nitrate, or magnesium nitrate.

However, because the gum arabic film on the non-image areas of the plate usually wears off gradually as the plate runs on the press, it is essential to introduce chemicals into the fountain solution which will rebuild this desensitiz-The most important ingredient for the activity of ing film. fountain solution is the desensitizing gum. Other ingredients are added to improve the adherence of the desensitizing gum to the non-image area of the plate. The acid portion of the solution converts the desensitizing gum into the free acid form which contains carboxyl groups (-COOH). It is assumed that these carboxyl groups cause the gum to adsorb to the metal surface of the plate.³ It is this adherence of the gum that causes the non-image to accept water. Ammonium bichromate or nitrate salts are added to act as corrosion

inhibitors.

One of the most widely used components of the fountain solution of offset-lithographic printing is gum arabic, a naturally occurring polysaccharide containing calcium, magnesium, and potassium ions. Gum arabic comes from acacia trees in the Middle East and North Africa. The type preferred in lithography is called "Select Gum Arabic Sorts."⁴ Gum arabic and other gums used as desensitizers in lithography are polyelectrolytes which are subject to the effect of other ions in the solution.

Lithographic inks tend to adhere to the non-image areas. The adhesion at the interface water/non-image areas should be, ideally, zero.⁵ The non-image areas are usually not sufficiently lipophilic to provide the ideal zero situation. To support the adhesion of the fountain solution to the non-image areas, a desensitizer is needed. The ink will adhere sufficiently to the image areas while the fountain solution forms a continuous film on the non-image areas to avoid scumming.

> "If the affinity to water changes, the tension at the interface water/non-image areas increases relative to the tension at the interface ink/non-image area, and water film will be displaced by ink film. Practically, it occurs when the desensitizing monolayer is mechanically abraded, and the metal surface becomes susceptible to contamination with oleophilic compounds."⁶

The effect of different ingredients in fountain solutions for the efficiency of dampening has been studied since 1776.

> "Research proved that alcohol can increase the adsorption of gum arabic to the plate. However, when the pressman

has little or no alcohol control, he may find out that excess alcohol will reduce the solubility of gum arabic, and the gum deposits on the image area of the plate. The gum deposit will cause image blinding. This is a danger that a pressman must be aware of. Excess alcohol will cause other problems that could create plate makeovers."⁷

Gum arabic was used as a desensitizer by Alois Senefelder to preserve lithographic surfaces in 1796. He found that:

> A few drops of gum arabic, dissolved in water, if applied to a wellpolished stone, produces the effect such that the spot thus wetted will not take ink, as long as it remains wet. As soon as it becomes dry, the ink adheres to it, but is easily wiped off with a sponge and water."⁸

Gum, besides being used as a densitizer on the plate surface and as a basic ingredient in the fountain solution, will combine with a dichromate in alkaline solution and thus makes a light-sensitive coating on the plate.⁹ Also, it can be made into an emulsion with asphaltum or other greasy materials to produce a one-step washout and gumming solution.¹⁰ Gum arabic is used to formulate lacquer developers required to process wipe-on and additive-type presensitized plates. It is used as a sizing and finishing agent in textile printing. Other applications include the food industry and pharmaceutical industry where gum arabic acts as an adhesive medium. The following terms are used in this chapter. The definitions of those terms are:

Resolution: Resolution is the ability to produce fineness of detail. Rhodes defined resolution as the ability of a system to resolve or discriminate between closely spaced elements.¹¹ Resolution can be affected by fill-in or slur. The resolution test object, which has liner perpendicular to sheet travel on the press, is affected by slur more than those parallel with sheet travel.¹² Good resolution is very necessary and important in printing halftones and fine detail.

Printing Sharpness: This refers to the relative change in dot size which occurs during the printing process. If the dot size on the printed sheet is approximately the same as the dot on the printing plate, it is considered that the print is sharp. Warren L. Rhodes proposed an objective measure of sharpness in 1955 and the Rhodes sharpness value was found to correlate with the visual impression of the spreading of dots.¹³ Rhodes sharpness value is obtained from the equation below:

> Rhodes Sharpness Value = Density of solid Density of tint

The printing sharpness will decrease if the density of the halftone tint increases. Fill-in and slur are assumed to be the main variables that affect sharpness. If we use Rhodes sharpness value to determine printing sharpness, a higher value indicates increased sharpness. If we divide the tint density by solid density the result would be opposite; that is, the lower the sharpness, the better.

Dot Size Change: A dot is the individual element of a halftone. Whenever the dot size of the reproduction is

bigger than the original on the printing plate, the size is assumed to have increased. Dot size change occurs at any pre-press stage as well as on the press. Coarse screen tints are less sensitive to dot size change than the finer screens.¹⁴ Dot size change affects the halftone density of the printed sheets.

The relative dot area of a printed sheet can be calculated by the Yule-Neilsen equation.¹⁵ This equation was derived from the Murrey-Davies equation in 1951 by Yule and Neilsen.¹⁶

> Yule-Neilsen equation: $D_t = -n \log (1-A(1-antilog(-\frac{Ds}{n})))$

Where: D_+ = Tint density

n = Correcting factor

 D_{s} = Solid density

A = Relative dot area of printed sheet or the effective dot area

To solve for relative dot area, the density values are converted to reflectance values and the equations below are obtained.

$$A = \frac{1-R_{t}}{1/n}$$

$$A = \frac{1-R_{t}}{1/n}$$

$$A = \frac{1-R_{t}}{1/n}$$

$$R_{t} = Reflectance of the tint$$

$$R_{r} = Reflectance of the solid$$

This equation is used to calculate the effective dot size area.

Surface Tension: The surface tension of a liquid, δ , is the force per centimeter on the surface of a liquid which opposes the expansion of the surface area.¹⁷ The contact angle of surface tension is zero when the liquid completely wets the ring. Contact angle is defined as the angle formed by the surface and a line drawn tangent to the liquid drop at its intersection with the surface.

The equation derived is:

$$\chi = \frac{f}{2L}$$

- λ = The surface tension of a liquid.
- f = The force pulling on a movable bar against a liquid film which is stretched like a soapbubble film on a wire frame.
- L = The length of a bar in centimeters, and the factor 2 is introduced because there are two liquid surfaces, one at the front and one at the back.

Viscosity: The resistance which a liquid exhibits to the flow of one layer over another. The viscosity of a liquid can be determined directly in poises by passing a liquid through a tube of small diameter and making use of the following formula:¹⁸

$$\eta = \frac{P \pi r^4 t}{8 v L}$$

 η = viscosity

- P = pressure applied
- t = time required for v ml of liquid to flow through a capillary tube of length L and radius r

Emulsification: When the interfacial tension between ink and water becomes low, small particles of ink may readily enter the dampening solution; this results in the occurence of emulsification of ink and scumming or tinting of the printing plate.

Statement of the Problem

As a result of drought-induced crop failures,

dislocations in the distribution system, energy crisis and inflation, shortages cause the likelihood of serious problems. Thus, natural resources become interrupted in the distribution system, irreplaceable decreases occur in labor, productivity failure, and increase in world consumption occurs because of war and international politics. This problem effects the printing industry, especially in lithographic printing because nearly all plate-press room chemicals come from natural resources. Gum arabic, is a naturally occurring polysaccharide from the Middle-East, North Africa, and Nigeria. It is gathered from the trees by natives, separated from the bark and sand, graded, and packed for shipment.¹⁹ Gum arabic dissolves readily in water and its polysaccharide nature is composed of calcium, potassium and magnesium salts of arabic acid. A cation exchange resin converts the gum arabic from its "salt form" into the "free acid form" called arabic acid.²⁰ The equation below explains the reaction.

(XCOO) ₂ Ca +	2HR =	2 1 COOH +	CaR ₂
one "salt form"	cation	arabic acid or	converted
of gum arabic	exchange	"free acid form"	exchange
	resin		resin

However, because the use of gum arabic is rising, continued shortages have inflated its retail price from \$3 to \$5 per gallon; it now passes the \$10-per-gallon mark.²¹ The problems of higher prices and shortages of gum arabic make it necessary to develop substitutes. Research proved that sodium silicate provides complete desensitization of metal surface after three hours immersion.²² However, if used in excess, it promotes ink emulsification and must therefore be used in quantity not exceeding 0.01 percent.²³ Cellulose gum is less susceptible to bacterial deterioration than gum arabic and, for this reason, is a more suitable material to use but it requires a higher concentration of 4 grams per litre to obtain a minimum contact angle. Gum arabic is used for the preservation of non-image areas against scratches during storage. If observed closely, it could be concluded that some of this aged desensitizing gum dissolves in the ink and gives rise to catch up, higher surface tension, and contact angle. Also, it is commonly observed that gum arabic is limited in its effectiveness depending on the condition of the plate surface.

Therefore, the addition of silicic acid in the fountain solution could possibly ameliorate the problems of gum arabic. Silicic acid is grouped among the water-soluble resins. It is safe to use, non-volatile as opposed to isopropanol or other water-soluble alcohols, has a very low molecular weight, is tacky, and is adhesive-like as a clear viscous liquid resembling glycerine. It can polymerize to a hard silica gel immediately when exposed to atmospheric moisture. It is assumed from the structure of silicic acid that the polymeric form carries hydroxyl groups. Silicic acid will cause water to show an extremely low contact angle on many surfaces. Silicic acid may cause image blinding after many impressions but this problem may be controlled by careful use.

Equation:

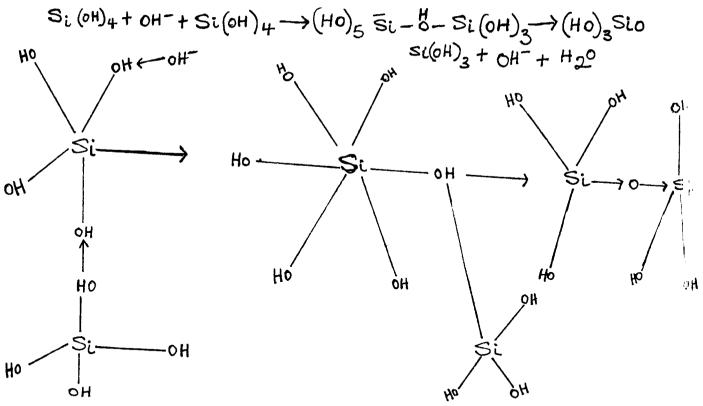
 $Li_2SiO_3 + 2H^+ \longrightarrow H_2SiO_3 + 2Li^+$ n(H_2SiO_3)--->Polymer

Silicic acid solubility and emf measurements demonstrate that the acid is diprotic and dissociates in two steps: 24

 $Si(OH)_4 + H_2O \longrightarrow SiO(OH)_3 + H_3O^+pk_1 = 9.8(20^{\circ})$

 $\text{SiO(OH)}_{3}^{-} + \text{H}_{2}^{0} \longrightarrow \text{SiO}_{2}^{-}(\text{OH})_{2}^{-} + \text{H}_{3}^{0}^{+}\text{pk}_{2}^{-} = 11.8(20^{\circ})$

The polymerization of silicic acid is catalyzed by OH⁻ ion as pointed out by Fleming in Ralph K. Iler's text.²⁵ Also, the polymerization of silicic acid may involve a temporary increase in the coordination number of silicon from 4 to 6, the additional sites being oxygen and hydroxyl ions. The equation below describes the reaction:



Silicic acid is one of the few available water-soluble resins which has not been studied as a gum arabic substitute in lithographic printing. Silicic acid properties as discussed made it a material for study.

The Purpose

The purpose of this study is to determine how effective silicic acid is in the fountain solution as a substitute for gum arabic. The response variables involved are surface tension, wettability, viscosity, dot size change, resolution, resistance to scum, blinding of plate, minimum dampening rate to clean-up the plate, performance distinction between lithium silicate and sodium silicate and changes with aging in solubility properties of silicates in fountain solutions.

Surface tension, wettability, and viscosity are measured physically with different instruments designed for each element. Test conditions are controlled throughout the experiments. The effectiveness of the solution to clean non-image areas of prints, dot size change, resolution, resistance to scum, blinding of image areas, and rate of de-inking over-run non-image areas are measured on the press. The comparisons are carried out under equivalent press conditions: ink, plate, paper. The only variables are one ingredient of the fountain solution and pH level.

The Hypothesis

The hypothesis is that if one adds silicic acid to the fountain solution as a substitute for gum arabic under equivalent press conditions, then plate desensitization would be achieved for better printing results. Although silicic acid should work as a desensitizing agent, one must look at the rest of its properties, and then determine how effective it would be since there are possible serious drawbacks.

Silicic acid may polymerize to form long chains. These later could form a precipitate which would separate from the rest of the solution. Thus, silicic acid may lose its effectiveness as a desensitizing agent, because the acid has decreased in solubility. These are determined by wettability, surface tension, viscosity, the ability of the solution to clean the plate, resistance to scum, printing sharpness, and resolution. ¹Michael H. Bruno, "Dampening: Lithography's Oldest Problem," Modern Lithography, <u>Vol.30</u>, (October 1962).

²W.H. Banks, "Why Does Lithography Work?" British Printer (July 1970): p.108.

³Paul J. Hartsuch, <u>Chemistry of Lithography</u>, (Pennsylvania: Graphic Arts Technical Foundation Inc., 1961) p.300.

⁴Robert F. Reed, <u>Offset Lithographic Platemaking</u>, (Pennsylvania: Graphic Arts Technical Foundation Inc., 1967) p.ll.

⁵Kurt Schlapfer, "Wettability Phenomena and Their Significance in the Lithographic Printing Process," 13th International Conference of Printing Research Institute (IARIGAI) Vol.13, (May 1975).

⁶Ibid., p.16.

⁷Eugene C. Bulinski, "Offset Lithographic Platemaking: Alcohol in Conventional Dampening," Graphic Arts Monthly, <u>Vol.44</u>, No.9, pp.120, 122. (Sept. 1972).

⁸A. Hyatt, ed., <u>A Complete Course of Lithography by</u> <u>Alois Senefelder</u>, (New York: Da Capo Press, 1968), pp.146-147.

⁹Albert R. Materazzi, "Lithographic Chemical Shortages Part I," Graphic Arts Monthly, (February 1974): p.88.

10_{Ibid}.

¹¹Warren L. Rhodes, "Study of Objective Methods for Evaluating Sharpness in Lithography," <u>TAGA</u> <u>Proceedings</u>, 1955 pp.109-122.

¹²Ibid., sample

¹³Ibid., sample

¹⁴Frank Prencil, Zenon Elijew and Robert F. Reed, "The GATF Dot Gain Scale," <u>GATF Research Progress</u>, No.69, pp.1-4.

¹⁵"Measurement of Dot Area," pp.1-2.

¹⁶J.A.C. Yule and W.J. Neilsen, "The Penetration of Light Into Paper and Its Effect on Halftone Reproduction," <u>TAGA</u> <u>Proceedings</u>, 1951, pp.70-72.

¹⁷Farrington Daniels, <u>Outlines of Physical Chemistry</u>, (New York: John Wiley and <u>Son: Inc.</u>, 1948), p.184.

¹⁸Barr's "A Monograph on Viscometry," <u>Outlines of Phys-</u> <u>ical Chemistry</u>, (Oxford University Press, Oxford, 1931), p.187.

¹⁹Paul J. Hartsuch, <u>Chemistry of Lithography</u>, (Pennsylvanic: Graphic Arts Technical Foundation Inc., 1967) p.130.

²⁰Ibid., pp.130-131.

²¹Lane Olinghouse, "Gum Arabic Substitutes Can Reduce Printing Production Costs," <u>In-Plant</u> <u>Printer</u>, (July/August 1975): p.40.

²²Bruce E. Tory, <u>Offset Lithography</u>, (Australia: Korwitz Publications Inc., 1957), p.74.

²³Ibiā., p.74.

²⁴S.A. Greenberg, "The Chemistry of Silicic Acid," Journal of Chemical Education, <u>Vol.36</u>, No.5, p.218 (May 1959).

²⁵Ralph K. Iler, "The Colloid Chemistry of Silica and Silicates," Polymerization, Cornell University Press, Ithaca, New York: p.38, (1955).

REVIEW OF LITERATURE

Dampening system design has been mostly that of applying a water film to the offset plate. However, since a press consists of cylinders or rollers, it seemed logical to roll the fountain solution on. A trouble-free lithographic printing press will require balancing of oleophilic and hydrophilic properties of the plate-ink-water system. Careful applications of surface chemistry are involved in separating the ink-receptive areas from the water-receptive areas. This includes the surface characteristic of the plate itself, the treatment of the plate surface, the component parts of the fountain solution and the general behavior of water and oil when they interact in a press operation.

Since the advent of lithography by Senefelder, many explanations of the lithographic phenomenon have been erroneous and lacking any experimental proofs. In 1928, we find the Lithographic Technical Foundation postulating views about the desensitizing role of "insoluble water-absorbent" films of gum arabic. The first scientist who carried out an experimental approach was G.L. Riddle. Riddle sought to establish experimentally that gum arabic was absorbed on lithographic surfaces thereby rendering them oleophobic.¹

A further experimental investigation was undertaken by F.J. Tritton who showed how the measurement of contact angles of oils on lithographic surfaces could be used as a quantitative measure of oil repellency. The effect of various platemaking treatments were shown to have a marked effect on the contact angle of oils placed on them.²

In 1954, Henry A. Beecham³ carried out experimental measurements of the contact angle of a drop (H_2O) resting on a flat surface. In 1956, R.A.C. Adams (P.A.T.R.A.) studied

contact angles and their significance in lithographic research. Adams and Beecham asserted that:

> "The contact angle obtained is determined by the actual condition of the solid surface at the time of the experiment. In general, with regard to metallic solids. the surface will be "contaminated" with a film of some kind such as grease, oxide, corrosion product. which may greatly modify its attractive properties. Since, under practical lithographic conditions, the metal surface is subjected to the action of aqueous solutions, it is necessary to determine the contact angle relationship for the metals when they are being subjected to the simultaneous action of the two immiscible liquid phases (oil and water) rather than to determine the separate actions of these liquids. These contact angles can give a considerable amount of information on the corrosion and adsorption phenomena associated with lithography."⁴

This methodology is called "interfacial contact angle", a developmental method postulated by Tritton. The method was devised for studying the affinity of liquids to surfaces because changes in contact angle are a significant measure of the changes in the wettability of the surface on which the liquid rests. Generally speaking, this method has been used to carry out most research.

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Different platemaking treatments also have a marked effect on the contact angle of oil or grease placed on them.

F.J. Tritton⁵ asserted that, on the average, a desensitized plate has a lower contact angle than the sensitized plate. He further stated that it is possible that this difference is simply because of the surface film thickness produced by the desensitizer.

Dating back to 1946, Elton and MacDougall studied and evaluated their results on the grain of lithographic printing plates and confirmed that:

> Graining the surface areas of the plate increases the area of metal exposed, gives more latitude to reacting solutions to come into contact and therefore increases the rate of chemical reaction at the surface. This in itself confers a considerable degree of desensitization on the grained plate. The expression which relates the contact angle on a smooth surface (Θ S) to that on a rough surface (Θ R) of the same material is: $R = \frac{\cos \Theta R}{\cos \Theta S}$

This equation means that contact angles under 90 deg. are decreased on rough surfaces. When they are over 90 deg. they are increased.⁶

Roughening a lithographic plate is beneficial in holding the ink on the image areas and to prevent the ink sticking to the non-printing areas of the plate.

The Crucial Influence of Gum Arabic and Cellulose Gum

It has been stated that gum arabic droplets on

lithoplates are not effective in their desensitizing properties unless they are fanned dry. Two researchers named Reed and King of the Lithographic Technical Foundation of America, found that when gum droplets or films are dried down on solid surfaces, a certain quantity of the droplet becomes insolubilized by oxidation and cannot be washed away by water.⁷ These ideas were confirmed by the PATRA interfacial contact angle method.

MacDougall conducted studies on the influence of gum arabic and sodium carboxymethyl cellulose or C.M.C. However, the argument as to whether or not a gum be added to the fountain solution could be better settled by the observation of the interfacial contact angle; thus:

> The contact angle technique provides a suitable and convenient means of finding out whether, in fact, the presence of gum or C.M.C. in the fountain Solution has any desensitizing effect.⁸

Experiments were conducted and results from data showed that the addition of gum arabic to fountain solutions has a marked beneficial desensitizing action if the effective concentration of gum is maintained within the range of approximately 0.3 percent or more.⁹

The experimental data showed that gum arabic solutions, over a period of time, lost their power of reducing the contact angles. MacDougall explained that:

> In some cases gum solutions which, when freshly made, had reduced the contact angle to the 'equilibrium' value of about 22 deg. were found twelve hours later to have no observable effect on the desensitizing of aluminum surfaces. This

deterioration on storage was traced to the decomposition of the gum by bacteria and moulds. If 0.01 percent of the preservative 'Zephiran Chloride' (a long chain alkyl dimethyl benzyl ammonium chloride) is added to the gum solution while fresh its desensitizing effect is preserved intact over a period of more than three weeks.

Solution of C.M.C. behaved in a very similar way to gum arabic. Both showed a minimum contact angle. The concentration curves and C.M.C. solution reached a steady value at higher concentrations. The curves were reversible in the same way as gum, so that the desensitizing effect of C.M.C. is not permanent unless it is dried on the surface of the plate. The concentration at which the minimum in the contact angle concentration curve occurred was 4 grams per litre. In the dilute form, there is no deterioration effect on storage which occurred with the gum arabic solution. Because it is concluded that C.M.C. is much less susceptible to mould and bacterial deterioration than gum, from this point of view, C.M.C. would be a more reliable and reproducible fountain solution.

Bruce E. Tory,¹¹ in his published article, studied the effect of the concentration of substances in fountain solution. Adams and Lawson conducted an investigation on the effect of lithographic fountain solutions on plate scumming. They concluded that the concentration of substances in the solution is the important factor in the prevention of scum. It is further assumed that acidity (pH) is the main factor.¹²

Adams and Lawson, however, suggested that the fountain solution should contain minimum amounts of various

substances, even when the pH of the solution is as low as 3.8 or as high as 7.0.¹³ However, because the surface of the plate is corroded by acid, and because gum arabic and cellulose gum do not inhibit this corrosion, it is advised that acid and gum should not be used alone in the fountain solution. When acid attacks the plate surface, the strength of the acid will not stabilize until the reaction stops. Thus, some salts are added in the solution to reduce plate corrosion and to buffer the fountain pH. This idea was investigated and confirmed by Adams and Ullman, thus:

> "The investigators found that corrosion was directly related to fountain solution pH and that dissolved gum cannot inhibit corrosion. That is, the lower the pH of fountain solution the greater the amount of corrosion. However, it was found that in the presence of a certain minimum amount of bichromate, corrosion was inhibited with a solution of pH as low as 3.9.¹⁴

The principles of adhesion of chemicals and gum arabic state that:

1. Image areas possess a chemically adsorbed layer of organic compound that renders the surface waxlike in character.

2. Non-image areas hold a thick, strongly adsorbed layer of gum arabic or similar colloid which, in the adsorbed state, can swell and hold a large quantity of water.

3. There are adhesion forces between all types of matter. The presence of alcohol will reduce the surface tension of a dampening solution mixture, and thereby improve the background wetting of the plate.

A high concentration of acid runs in from the edges of image areas and undercuts them. The undercutting on the image areas reduces dot size until the fine highlights disappear from the plate. Stewart¹⁵ asserts that increasing the amount of acid will not keep the non-printing area clean instead, it often makes the background area sensitive and even more receptive to ink. The result is scumming and toning. However, the water feed rate in lithography can be decreased by properly desensitizing the plate surface and/or with a low surface tension of the fountain solution.

The Mechanism of Fountain Solution - Air Boundary in Lithography

Because of the surface active nature of the ink vehicle, lithographic inks shed films of oil onto the water with which they are in contact. These films are of molecular dimension in thickness and, when deposited on the plate, they spread across the boundary between the inked image and the adjacent desensitized areas. Present understanding of the mechanism of lithography is derived mainly from the early work of R.A.C. Adams at PATRA.

> "Adams identified that the characteristic properties of the printing surface determines the preference for ink or for water. The principles established were necessarily concerned with the situation at the boundary between plate and water on the one hand and ink on the other when all three components are brought together. In this context the situation at the fountain solution/air boundary are relevant."¹⁶

The boundary assumes importance when the dampening solution evaporates, as for example, during press stop. Evaporation of the water from these areas therefore, will result in accumulation of ink on the metal with a consequent sensitizing of the non-image area. It may also play a part in the accumulation of ink on the dampening rollers, although, to date, there is no definite supporting evidence.¹⁷ Continuous printing without the intervention of the usual treatment with gum arabic solution can result in an overall scumming and toning.

The paper presented at the annual conference of the printing industry of America on May 29, 1968 by W.H. Banks, A.H. Smith, D.H. Charlesworth reported that:¹⁸

1. The spreading is controlled by the surface tension of the aqueous layer;

2. All films or droplets likely to spread from inks as now constituted, can be prevented from doing so when the surface tension of the aqueous solution does not exceed 36 dynes/cm^{-1} .

3. Monolayers of oleic acid are sufficient to sensitize a plate.

This lead us to conclude that the surface tension plays an important role thus:

> The effect of surface tension on the spreading of films is independent of composition of the fountain solution, and films cannot form when the surface tension is about 37 dynes/cm. Thus, as with pH, the control of surface tensions should now be regarded as a general requirement of all fountain solutions irrespective of their formulation.¹⁹

¹W.H. Banks, "Some Physio-Chemical Aspects of Lithography," <u>Proceedings of the First Conference</u>, <u>Association of</u> Printing Technologists (1957): p.16.

²Ibid.

³Henry A. Beechem, "Contact Angles," Offset-Litho Chemistry, GAM, Vol.26, pp.64, 66 (Dec. 1954).

⁴R.A.C. Adams, "Contact Angles and Their Significance in Lithographic Research," <u>International Bulletin for the</u> <u>Printing and Allied Trades 73</u>, (January 1956): 23.

⁵F.J. Tritton, "A Study of the Theory of Lithographic Printing, Part I," <u>Journal of the Society of Chemical</u> <u>Industry</u> 51, (September 2, 1932): p.303.

⁶G.A.H. Elton and G. MacDougall, "The Evaluation of the Roughness of Lithographic Printing Plates," Journal of the Society of Chemical Industry 65, (July 1946): pp.212-215.

⁷G. MacDougall, "Some Comments on the Desensitization of Lithographic Plates," The Penrose Annual (1949): p.126.

⁸Ibid.

9_{Ibid}.

¹⁰Ibid., pp.126-127.

¹¹Bruce E. Tory, Offset Lithography, (Australia:Korwitz Publications Inc., 1957): p.75.

¹²Ibid.

13_{Ibid}.

¹⁴C. Stewart, "Fountain Solution," The Litho Printer, <u>Vol.3</u>, p.172, (April 1960).

¹⁵W.H. Banks, A.H. Smith, D.H. Charlesworth, "A Development in the Theory of Lithographic Fountain Solutions," Printing Trade Journal, (July 1968): p.117. ¹⁶Ibid. [•] ¹⁷Ibid. ¹⁸Ibid.

METHODOLOGY AND RESULTS

If silicic acid is added to the fountain solution (as a substitute for gum arabic), better desensitization on plates, and good quality prints will be achieved. The variables during the experiments were controlled. The tests were conducted in two parts:

Part I: The test of physical properties of both solutions.

Part II: The press performance or printed results.

The response variables tested included surface tension, wettability, viscosity, dot size change, resolution, resistance to scum, blinding of plate, minimum dampening rate to clean-up the plate, rate of de-inking over -run non-image areas, performance distinction between lithium silicate and sodium silicate, and changes with aging in solubility properties of silicates in fountain solutions.

Gum arabic, lithium polysilicate and sodium silicate were supplied in solution. They were also measured by volume/volume. Gum arabic solution, as recommended by the manufacturer, 3M Company, was one ounce of 14 Baumé Gum Arabic, one ounce of Fountain Concentrate and one gallon of water. Silicic acid was prepared by treating a silicate solution with an acid. Silicic acid solution was prepared and the preliminary test was made using different concentrations at different pH levels. The concentration ranged from 2cc to 25cc/100cc of water. Phosphoric acid was used to vary the pH of both fountain solutions. The press and other testing conditions were kept constant. The controlled variables and test conditions are shown in Appendix A.

TEST PROCEDURE

This study considered a relatively wide range of characteristics and, as such, the test procedures were different from one to another. In each case, however, the conditions of the test and all variables that applied to both silicic acid and gum arabic were the same

Part I - The Physical Property Test

Surface Tension: To determine the surface tension of the solutions, a du Nouv Tensiometer. Ring Method was used. The surface tension relates to the force required to detach a metal ring from the surface of a liquid.

The tensiometer was calibrated according to the manufacturer's instructions. The standard weights of lgm, 2gms, and 3gms were used for calibration. The dial reading called "gamma-c" was then calibrated as the following equation."

$$\gamma = \frac{K\overline{X}}{2L}$$

Where

 χ = surface tension

K = gravity constant (note 1), in Cgs. units and X = weight placed on the metal platform in centimeters L = means length of the copper bar in centimeters, and factor 2 is introduced because there are two liquid surfaces, one at the front and one at the back

Therefore

$$\chi = \frac{K\overline{X}}{2T}$$

Silicic Acid Gum Arabic $y = \frac{7.80 \times 980 \times 8.33}{2 \times 7.00} \qquad \qquad y = \frac{7.80 \times 980 \times 5.60}{2 \times 7.00}$

 $\mathcal{X} = 45.48 \text{ dynes/cm}$ $\mathcal{Y} = 30.58 \text{ dynes/cm}$

(Note 1: The gravity constant is 980.3 at Chicago; in other locations it will differ very slightly from this value).

Results:

The surface tension of silicic acid and gum arabic were measured at different concentrations and pH levels. The mean was obtained from five values. The results showed a significant difference in the surface tension of various silicic acid solutions. The surface tension ranged from 28.09 to 48.32 dynes/cm. The surface tension of silicic acid increases with concentration while the pH levels remained fluctuating, figure III.

Table I

Relationship Between Surface Tension and Concentration of Silicic Acid Solution

Concentration ofSurface Tension (dynes/cm) atsilicic acid *different pH levels and with astandard deviation (+1.0)

			pH = 3.5 - 3.8	4.0-4.5	5.0-5.5	5.8-6.7
*	*	2.00	33	30	31	28
×	×	3.00	34	31	30	28
×	×	5.00	32	33	32	28
×	*	9.00	35	36	35	30
¥	*	11.00	36	37	36	48

* Solution prepared by dissolving 25cc of sodium silicate (supplied as "waterglass" by Chemical Sales Corp.) plus 10gms of lithium chloride (supplied by Fisher Scientific) plus 15cc of 85% H₃PO₄ plus 20cc of isopropanol in 300cc of de-ionized tap water.

** Silicic acid solution diluted in parts per 100cc of water

The surface tension of gum arabic was highest at the 1.0 oz/gal concentration. Gum arabic solution of 0.1 oz/gal had a surface tension of about 45-58 dynes/cm. However, it should be noted that as the concentration of gum arabic increases the surface tension also increases. Figure 4.

Comparing silicic acid solution to gum arabic solution, the surface tension of silicic acid was lower than that of gum arabic. The 14° Baume gum arabic solution had a surface tension of 60.88 dynes/cm while water had 73.89 dynes/cm. The data are shown in Table I and Table II.

Table II

Relationship Between Surface Tension and Concentration of Gum Arabic Solution

Concentration of Fountain Solution* Surface Tension dynes/cm pH = 4.5-5.0

0.1	45.48
0.4	50.35
0.6	57.48
0.8	75.69
1.0	80.58
1.2	78.43
1.4	79.44
1.6	79.48
1.8	74.78
2.0	72.44

* Prepared by dissolving l oz of 14 Baumé gum arabic solution (Anchor Chemical Co., Inc.) plus l oz 3M Fountain Concentrate (3M Products) per gallon of de-ionized tap water. Contact Angles: 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 1., the contact angle is defined as the angle 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 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.

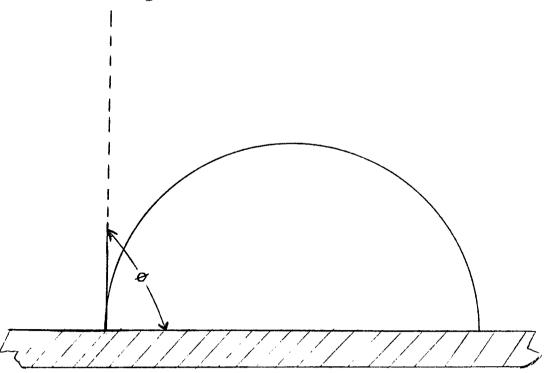


Figure 1. Contact Angle

If, in fact, the plate is very water receptive as indicated by a low contact angle, then it must be true that the plate attracts and holds varying quantities of water to various areas of the plate.

To determine the contact angle of silicic acid and gum arabic solutions, an Optical Comparator Projector was used. Strips of small metal plates 4 x 2 cm were carefully cleaned and used. The Optical Comparator Projector was calibrated by turning on the light and bringing the edge of the metal plate into focus with a protractor scale which read 0° on one edge and 180° on the other edge.

A drop of the solution was then squeezed from a straight pipette held over the plate surface on each strip of the metal plate. An enlarged silhouette of the drop was projected onto a screen by the use of a light source and lens arrangement. The width and height of the drops, as projected, were measured with a protractor scale. From these two measurements. the contact angle was determined using the formula derived in Figure 2. Measurements of solutions with different concentrations were carried out in random order. Three measurements were taken on each sample solution and their mean gave an approximation of expected reading. A drop may be regarded as held in equilibrium by balancing of three forces (vertical, horizontal and angular) acting at right angles to the line of contact of the three interface and in the planes of the interface.²

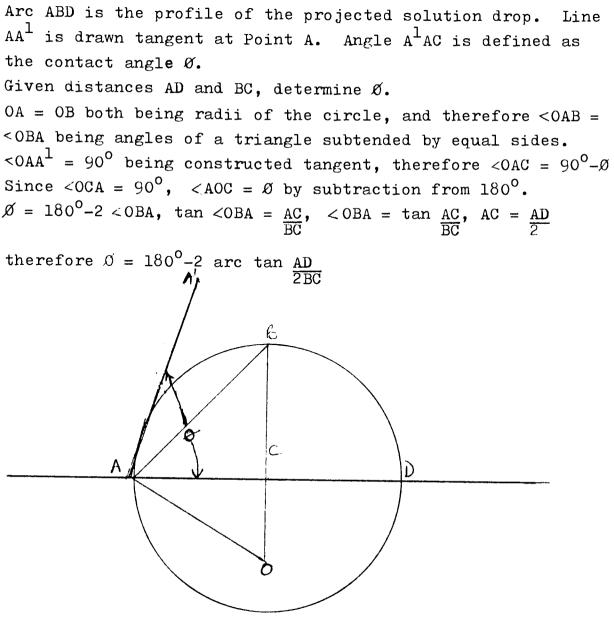


Figure 2. Contact Angle Calculation³

Results:

The contact angles of silicic acid and gum arabic were measured at different concentrations. The mean obtained from five values of different gelling time did not show any significant difference in the contact angle of various silicic acid solutions. (See Table III) Silicic acid solution wets the plate so rapidly that, within a second, it

spreads over the plate surface. The contact angle ranges from 1.5° to 6° , Table III.

Table III

The Contact Angle of Silicic Acid Solution at Different Concentration and Gelling Time

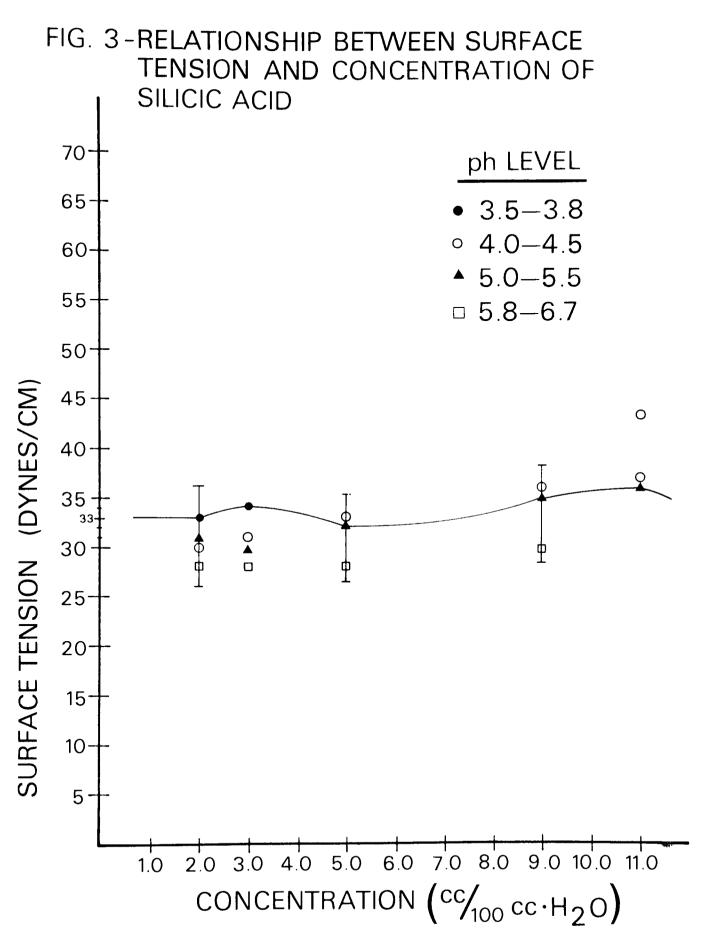
Concentration of	Contact	Angle (Degree)	at	
Silicic Acid *	Different Gelling Time				
	2 days	3 days	3 days	4 days	
2.0	2 ⁰	1.5 ⁰	2 ⁰	2 ⁰	
3.0	2.5 ⁰	2 ⁰	2.5 ⁰	3°	
5.0	3 ⁰	2 ⁰	2.5 ⁰	3°	
9.0	4 ⁰	3•5°	4.5 ⁰	4 ⁰	
11.0	5.5 ⁰	4.5 ⁰	5.0 ⁰	6 ⁰	
* See page 26					

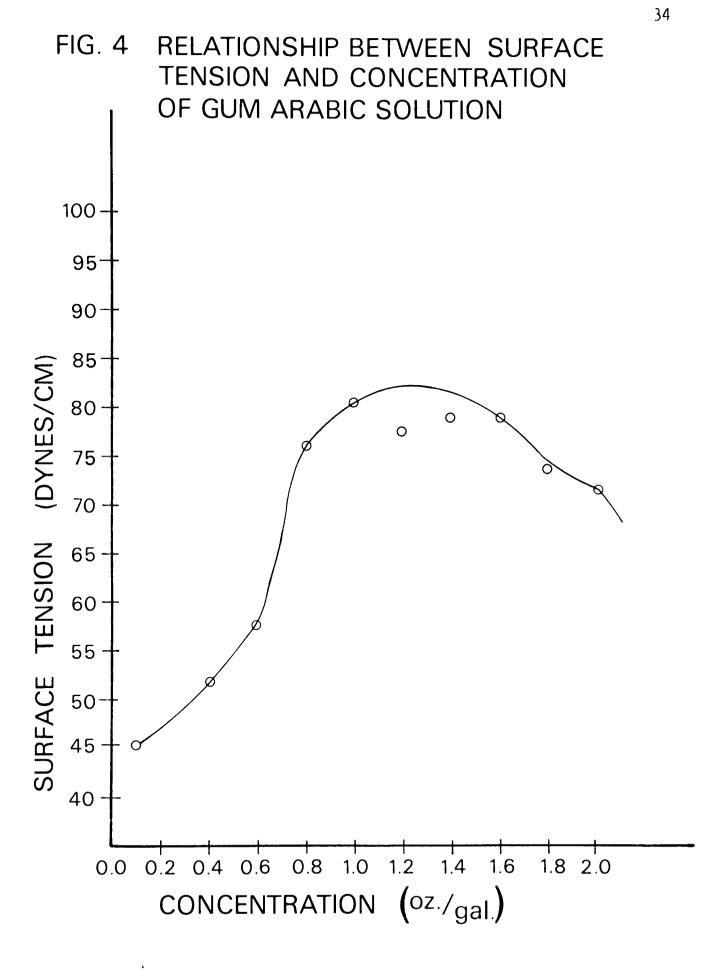
The contact angle of gum arabic solution at 0.1 oz/gal was about 15° , Table IV. It was observed that the larger the drop, the smaller the contact angle. Comparing silicic acid to gum arabic solution, the contact angle of silicic acid was lower than that of gum arabic. Also, the contact angle of silicic acid increases with concentration while the contact angle of gum arabic decreases with increased concentration, Figures 5 and 6.

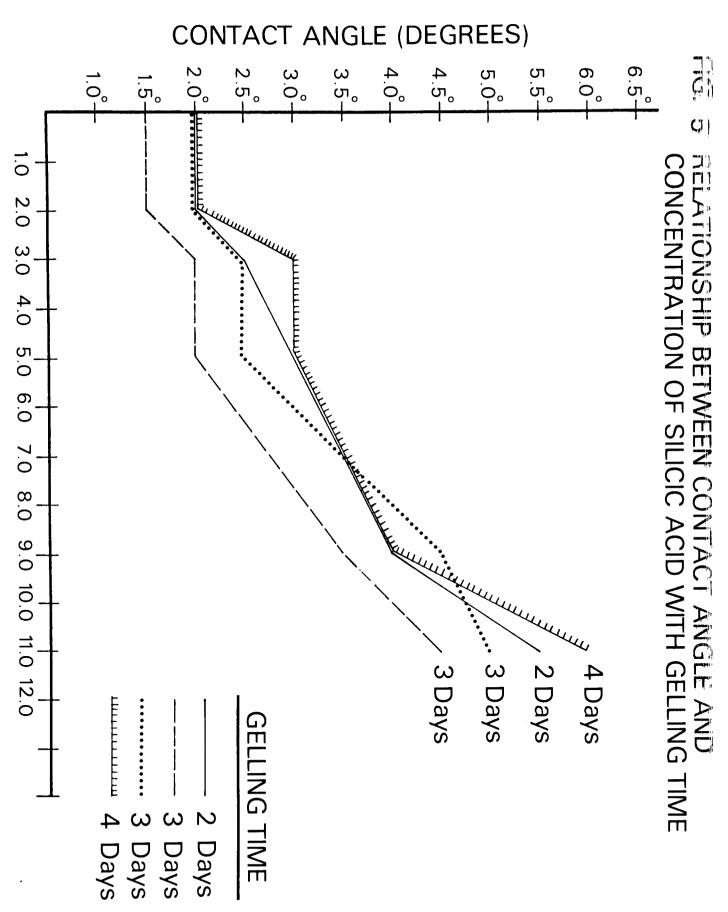
Contact Angle of Gum Arabic Solution

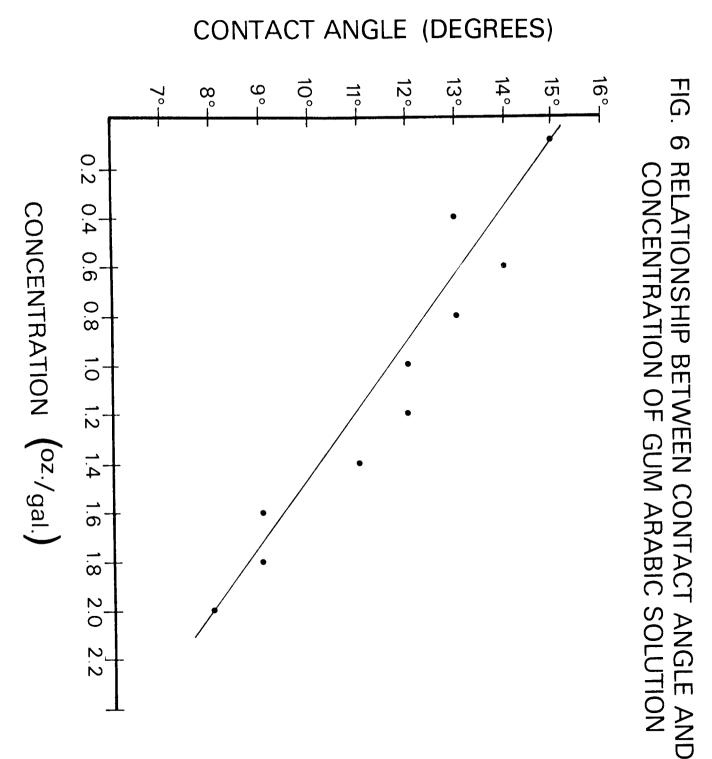
Concentration of	Contact Angle
Fountain Solution *	(Degree)
0.1	15 ⁰
· 0.4	13°
0.6	<u>1</u> .4 ⁰
0.8	13°
1.0	12 ⁰
1.2	12 ⁰
1.4	llo
1.6	9 0
1.8	9 0
2.0	8°

* See page 27









Viscosity: Viscosity may be defines as:4

Viscosity = <u>Shear stress</u> Rate of shear

It is also the resistance which a liquid exhibits to the flow of one layer over another.

The viscosity of the solutions was measured by the Brookfield Synchro-Lectric Viscometer, Model RVT. The viscometer measures viscosity by measuring the force required to rotate a spindle in a fluid.

The property of the desensitizer was a factor and therefore, the desensitizer alone was mixed with ink. Different concentrations of solutions were measured as shown in Table V and Table VI. These concentrations were mixed with 2 to 8 ozs. of ink, one at a time. The mixture of desensitizer and ink was blended for 20, 25, 30 and 35 minutes each. The amount of solution and the container for each measurement were controlled because viscometer ranges will generally change if a smaller or bigger container is used. According to the manufacturer, the Brookfield Viscometer is specified to be accurate to within $\frac{+}{2}$ 1.0 percent and to be reproducible to an area within $\frac{+}{2}$ 0.2 percent.

The viscosity value was obtained by multiplying each scale reading by the factor number given by the manufacturer's literature. In this test, the viscometer model RVT, spindle number A and B, speed 10, 20, 50, 100 rpm gives the factor number of 10, 20, 50, 100. Viscosity is expressed in centipoise (c.p.s.).

The instrument was operated according to the manufacturer instructions. Five scale readings were taken five minutes after the instrument was properly calibrated and started. The second, third, fourth and the fifth readings were taken three minutes thereafter. Results:

Silicic acid is in solution. As the rate of shear increases, the viscosity decreases Figure 7. The

concentration at 9.0cc silicic acid/100cc H₂O mixed with ink show a marked fall in viscosity from the pH of 4.5 to 5.0 For gum arabic solution, the viscosity increases as the concentration increases (Figure 8). The viscosity of de-

ionized water was about 4.0 centipoise while that of 14⁰ Baumé gum arabic solution was about 43 centipoise.

Table V

Relationship Between Viscosity and Silicic Acid Concentration						
Concentration of	Viscosity	(CPS) vs. B	lending Tim	e		
Silicic Acid */oz ink	20	25	30	35(minutes)		
** 2.00 per 7 oz ink	-		2.000x10 ⁴			
** 3.00 per 6 oz ink			1.052×10^{4}			
** 5.00 per 6 oz ink	-	. .	0.369×10^4			
** 9.00 per 4 oz ink	0.328x10 ⁴	0.329×10^{4}	0.332x10 ⁴	0.236x10 ⁴		

* Solution prepared by dissolving 25cc of sodium silicate (supplied as "waterglass" by Chemical Sales Corp.) plus lOgms of lithium chloride (supplied by Fisher Scientific) plus 15cc of 85% H₃PO₄ plus 20cc of isopropanol in 300cc of de-ionized tap water.

** Silicic acid solution diluted in parts per 100cc of water.

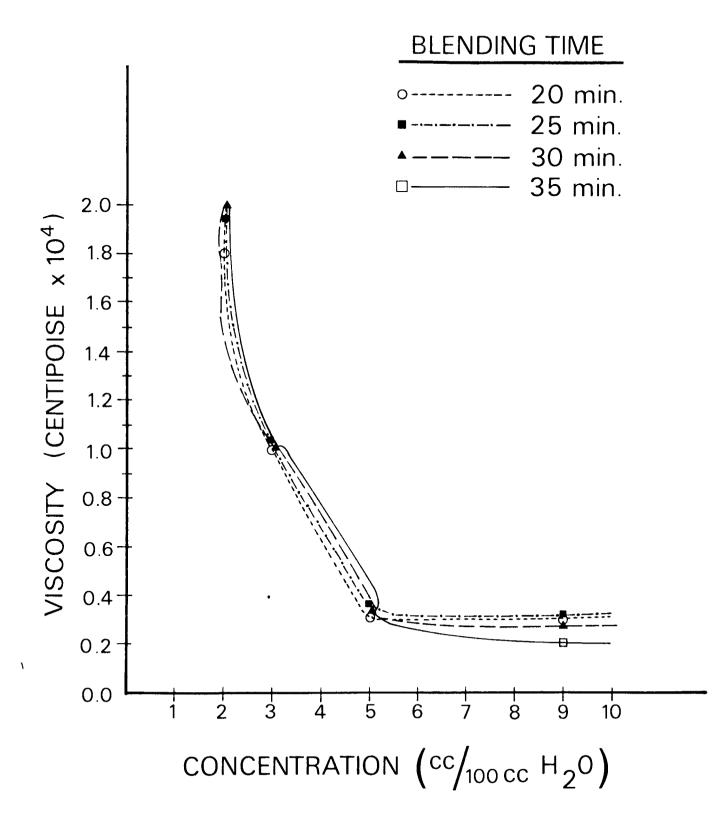
Relationship Between Viscosity and Concentration of Gum Arabic Solution

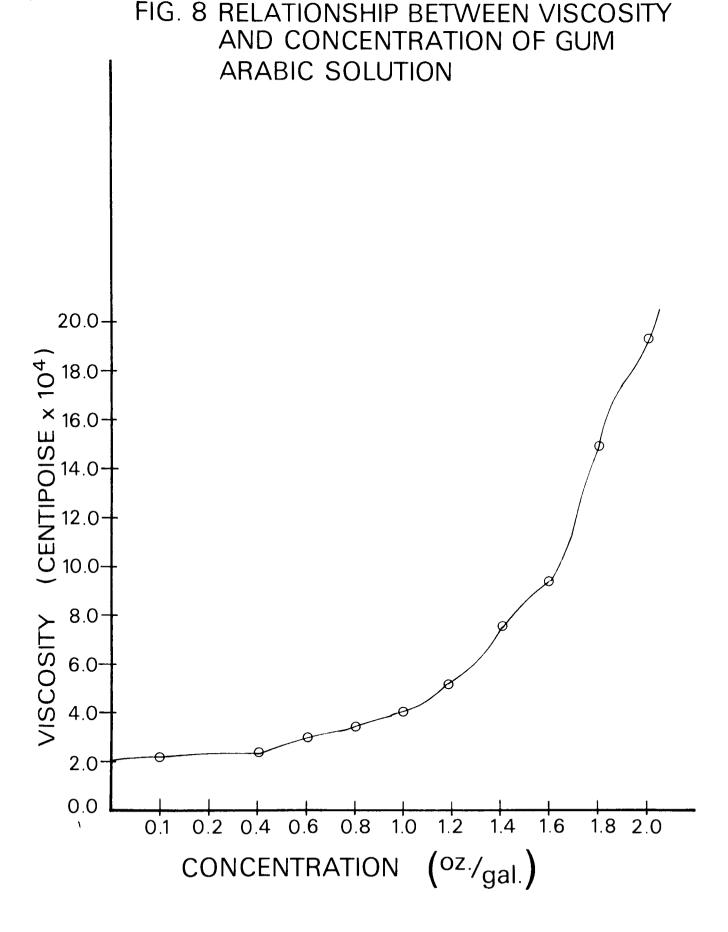
Concentration of	Viscosity
Fountain Solution *	(cps)
0.l per 2 oz ink	2.12x10 ⁴
0.4 per 2 oz ink	2.21x10 ⁴
0.6 per 3 oz ink	3.20x10 ⁴
0.8 per 3 oz ink	3.80x10 ⁴
l.O per 3 oz ink	4.00x10 ⁴
l.2 per 4 oz ink	5.02×10^4
l.4 per 5 oz ink	7.83x10 ⁴
l.6 per 6 oz ink	9.64×10^4
1.8 per 7 oz ink	15.00×10^4
2.0 per 8 oz ink	19.62x10 ⁴

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* Prepared by dissolving l oz of 14 Baumé gum arabic solution (Anchor Chemical Co., Inc.) plus l oz 3M Fountain Concentrate (3M Products) per gallon of de-ionized tap water.

FIG. 7 RELATIONSHIP BETWEEN VISCOSITY AND CONCENTRATION OF SILICIC ACID SOLUTION





Part II-Press Performance

To compare and evaluate the printed results obtained with each solution, tests were run with controlled variables such as press conditions, plate, blanket, paper, ink and pH of the fountain solution.

The conventional gum arabic solution used was prepared with one ounce of 14 Baumé gum arabic and one ounce of 3M Fountain Concentrate to a gallon of water. Silicic acid solution used was varied. The concentrations ranged from 2.0 cc to 25.0 cc sodium silicate with phosphoric acid and lithium chloride to 100 cc of water, and the gelling time ranged from 8 hours to 96 hours. Different concentrations were used one at a time on the press runs.

Different concentrations were tried and the concentration which gave fewest problems were used in the comparison with gum arabic solution.

Results showed that silicic acid at high concentration and low viscosity caused numerous problems on the press. The physical characteristic of silicic acid is gel-like when dissolved in water and allowed to settle for a few hours. At high concentration, the viscosity decreases. Silicic acid gels on the fountain solution pan surface. Because it formed a foam, the foam droplets of the fountain solution came in contact with the plate. It deposited some droplets on the surface of the ink rollers thereby causing slippage among ink rollers, emulsification, and tinting. Also, it blinds the image when too concentrated. The ink-water-balance seemed hard to control because the viscosity of the silicic acid solution was low. The gel-like solution could not desensitize the plate easily. The solution was diluted with water until this problem was under control and clean printed sheets were obtained.

Dot Size Change Test

Differences in solid ink density influence the tint

density values. A dot is the individual element of a halftone. Whenever the dot size of the reproduction is bigger than the original on the printing plate, the size is assumed to have changed. If there is slippage or excess packing squeeze between cylinders, or a poor ink-water-balance, the dot size will be affected and thereby result in unsharp reproduction.

Dot size change values are obtained by dividing the density of tint by the density of solid. The data refers to normal ink settings. High densities are possible by applying heavier films of ink. This is not advisable because it causes offsetting problems, slow ink-drying and clogging of shadows in halftone work.⁵ The data are shown in Table VIII through Table X. Two factors with two replicates is used as an analysis of variance. Table XI summarized the ANOVA Table. The statistical results show that the calculated value exceeds the table value: Rickmers and Todd.⁶ It is con-... cluded that there is a significant difference in the dot size due to changing the fountain solution. The gum arabic solution maintained the same dot size on a printed sheet as was on a printed sheet from what was on the plate. The dot size change may be attributed to a high concentration of sodium silicate and phosphoric acid in the silicic acid solution.

Table VII

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Dot Size Change Values of Prints From Gum Arabic Solution at Both High Ink Film Thickness (1.50[±]0.05 Density) and Low Ink Film Thickness (1.20[±]0.05 Density) Using 85% Tint

Sample of	High Ink Film	m Thickness	Low Ink Film	Thickness
Printed Sheets	Solid	Tint	Solid	Tint
	lst Run	2nd Run	lst Run	2nd Run
l	1.24	1.07	0.80	1.01
2	1.30	1.05	1.00	1.04
3	1.29	1.06	0.90	1.03
4	1.07	1.10	0.90	1.09
5	1.29	0.99	0.98	1.06
6	1.28	0.85	0.95	0.89
7	1.29	1.18	0.94	0.66
8	1.25	1.13	0.92	0.62
9	1.21	1.07	0.89	0.45
10	1.32	1.05	0.97	0.55
11	1.26	0.98	1.34	0.69
12	1.30	1.08	1.45	0.70
13	1.27	1.03	0.99	0.69
14	1.29	1.00	1.39	0.62
15	1.25	1.01	1.48	0.68
16	1.28	0.86	1.43	0.65
17	1.24	0.95	1.50	0.61
18	1.23	0.82	1.33	0.65
19	1.29	0.93	1.26	0.67
20	1.30	0.91	1.29	0.87
21	1.33	0.88	1.31	0.93
22	1.26	0.87	1.09	0.79
23	1.28	0.95	1.25	0.67
24	1.31	1.08	1.39	0.98
25	1.25	1.10	1.24	0.89
Total:	$\bar{X} = 1.27$	$\overline{X} = 0.96 \overline{X}$	= 1.16	0.78

Table VIII

Dot Size Change Values of Prints From Silicic Acid Solution at Both High Ink Film Thickness (1.50⁺0.05 Density) and Low Ink Film Thickness (1.20⁺0.05 Density)

Using 85% Tint

Sample of	High Ink Film	Thickness	Low Ink Film	Thickness
Printed Sheets	Solid	Tint	Solid	Tint
	lst Run	2nd Run	lst Run	2nd Run
1	1.35	1.25	1.50	1.11
2	1.36	1.19	1.40	0.70
3	1.17	1.33	1.42	1.12
4	1.36	1.29	1.40	1.12
5	1.20	1.41	1.43	1.10
6	1.09	1.32	1.51	1.11
7	1.34	1.19	1.45	0.90
8	1.27	1.28	1.47	1.14
9	1.34	1.20	1.48	1.22
10	1.35	1.29	1.44	1.07
11	1.30	1.39	1.43	1.03
12	1.31	1.33	1.40	0.89
13	1.38	1.32	1.39	0.79
14	1.49	1.33	1.35	1.53
15	1.50	1.39	1.45	1.01
16	1.49	1.31	1.45	1.49
17	1.48	1.29	1.42	1.45
18	1.49	1.26	1.38	1.48
19	1.49	1.33	1.37	1.45
20	1.45	1.32	1.31	1.43
21	1.50	1.39	1.36	1.40
22	1.50	1.30	1.26	1.29
23	1.39	1.31	1.26	1.06
24	1.37	1.33	1.43	1.01
25	1.46	1.29	1.53	1.08
Total:	$\bar{X} = 1.38$ $\bar{X} =$	1.31 X =	:1.41 X =	1.32

Dot Size Change Data From Two Fountain Solutions at Both High Ink Film Thickness (1.50-0.05 Density) and Low Ink Film Thickness $(1.20 \pm 0.05 \text{ Density})$ Using 85% Tint

Fountain Solution	High Ink Film	Low Ink Film	
	(1.50 ⁺ 0.05 Density)	(1.20 ⁺ 0.05 Density)	
Gum Arabic	1.27, 1.16	0.96, 0.78	
Silicic Acid	1.38, 1.41	1.31, 1.32	

Table X

ANOVA Summary Table for Dot Size

Source	Sum of sguares	Degree of freedom	Mean square	F ratio
Type of Solutions	0.1953	l	0.1953	34.2632 *
Solid Ink Density	0.0903	1	0.0903	15.8421 *
Interaction	0.0352	1	0.0352	6.1754 N.S.
Error	0.0228	4	0.0057	
Total	0.34355	7		

Critical F_1 , 4, .05 = 7.7086

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* Significant Statistical Difference

RESOLUTION

This is defined as the ability to produce fineness of detail. In this experiment, the RIT Alphanumeric test objects was used as a standard for the evaluation of the resolution of a printed sheet. Each of the four quadrants of the test object consists of 26 three-character groups ranging in size from 1 line/mm to 18 lines/mm, the progressive change in size following the sixth root of two. Each of the quadrants is individually randomized. (This presents some difficulty in that any observer using the target cannot read all 26 groupings for any given experimental condition. Therefore, the characters actually seen by the observer are not truly random).⁷

This target has been chosen to evaluate the resolution of a printed sheet despite claims that the alphanumerics used are not equally recognizable (Bobb,⁸ 1975), and are not truly random in their distribution. This author believes that the advantages gained by its use (inherent uncertainty, a reasonably close approximation to equal recognizability) will outweigh the shortcomings.

The characters (2, 3, 5, 8, E) were randomly composed in groups of three ranging in size from one line/mm for the largest to approximately 18 lines per mm for the smallest. The progressive change in (size) from one line to the next was by the sixth root of two.

A 10 power glass was used for the evaluation. The data are shown in Table XII through Table XIV. The data were analyzed by the two factors analysis of variance with two replicates.

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Table XV summarized the ANOVA Table. The analysis of the statistical results shows that the calculated value for F ratio did not exceed the table value. We then conclude that the error is so large that we cannot see any significant statistical difference in resolution caused by changing the fountain solution. Both solutions gave identical resolution. Resolution Values of Prints From Gum Arabic Solution at Both High Ink Film Thickness (1.50 ± 0.05) Density and Low Ink Film Thickness (1.20 ± 0.05) Density

Sample of Printed Sheet		Film Thicknes 2nd Run	s Low Ink 1 lst Run	Film Thickness 2nd Run
1	9.0	8.0	8.0	8.0
2	8.0	7.1	6.3	5.7
3	7.1	5.0	7.1	6.3
4	6.3	10.1	9.0	9.0
5	7.1	8.0	8.0	7.1
6	5.7	5.7	8.0	б.3
7	6.3	7.1	6.3	7.1
8	8.0	5.7	8.0	6.3
9	9.0	5.0	6.3	5.7
10	7.1	7.1	5.0	5.0
11	5.0	4.0	7.1	7.1
12	5.7	5.7	5.7	5.0
13	8.0	6.3	6.3	5.7
14	9.0	5•3	5.0	6.3
15	7.1	4.0	8.0	7.1
16	6.3	5.0	7.1	6.3
17	7.1	9.0	7.1	8.0
18	8.0	6.3	5.7	5.0
19	5.7	4.0	6.3	9.0
20	5.0	6.3	5.0	7.1
21	7.1	9.0	6.3	5.7
22	9.0	7.1	9.0	7.1
23	6.3	8.0	8.0	8.0
24	8.0	10.1	7.1	9.0
25	7.1	4.0	6.3	5.7
$\overline{\mathbf{X}}$ =	7.12 X	6.504	$\overline{X} = 6.504$	$\bar{X} = 6.384$
Sx	= 1.2203 S	x = 1.8901	$S_{x} = 2.5682$	$S_{x} = 2.5370$

Resolution Values of Prints From Silicic Acid Solution at Both High Ink Film Thickness (1.50⁺0.05) Density and Low Ink Film Thickness (1.20⁺0.05) Density

Sample of Printed Sheets	High Ink Film	Thickness	Low Ink Film	Thickness
	lst Run	2nd Run	lst Run	2nd Run
l	7.1	7.1	6.3	7.1
2	5.7	4.0	8.0	5.7
3	7.1	6.3	9.0	5.0
4	7.1	8.0	6.3	6.3
5	4.5	7.1	5.7	5.0
6	3.6	4.5	5.0	6.3
7	6.3	4.0	7.1	8.0
8	4.0	5.7	5.0	5.7
9	3.6	4.5	5.7	9.0
10	3.2	4.5	6.3	5.0
11	6.3	5.0	6.3	6.3
12	4.5	4.0	7.1	5.0
13	6.3	5.0	5.0	5.7
14	5.7	4.5	6.3	7.1
15	6.3	6.3	6.3	8.0
16	5.0	4.0	7.1	9.0
17	6.3	7.1	6.3	8.0
18	4.0	5.0	6.3	8.0
19	4.5	4.5	5.0	7.1
20	6.3	6.5	5.7	7.1
21	8.0	5.7	4.5	5.0
22	9.0	7.1	5.0	6.3
23	7.1	7.1	6.3	7.1
24	6.3	5.0	3.2	6.3
25	9.0	8.0	5.0	5.7
	$\overline{X} = 5.41$	2 x =	5.992 $\bar{X} =$	6.592
$S_x = 1.61$	18 $S_x = 2.1$	378 S _x	= 1.1867 S _x =	= 1.2433

Table XIII

Resolution Data From Two Fountain Solutions

at Both High and Low Ink Film Thickness

Fountain Solution	High Ink Film	Low Ink Film
	(1.50 ⁺ 0.05 density)	(1.20 ⁺ 0.05 density)
Gum Arabic	7.12, 6.504	6.504, 6.384
Silicic Acid	5.872, 5.412	5.992, 6.592

Table XIV

ANOVA Summary Table for Resolution

Source	Sum of squares	Degrees of freedom	Mean square	F ratio
Type of solutions	0.88	1	0.88	7.333 N.S.
Solid ink density	0.05	1	0.05	0.4166 N.S.
Interaction	0.51	l	0.51	4.25 N.S.
Error	0.48	4	0.12	
Total	1.92	7		

Critical F_1 , 4, 0.05 = 7.7086 No significant statistical difference

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RESISTANCE TO SCUM TEST

Scumming is defined as the adherence of ink to part of the non-image areas of a lithographic printing plate.⁹ Periodically, scumming is called "greasing." Scumming is caused by (a) an improperly formulated fountain solution; (b) a poorly desensitized plate; (c) a greasy ink which contains materials which can stick easily to the non-image areas of the plate; (d) possibly a paper with excess of alum and other ingredients in it.

However, because all the variables, especially press conditions, pH of the fountain solution, ink, plate, paper were controlled, the only variable present was the fountain solution. To test the resistance to scum, silicic acid solution was run on the press. The press was adjusted until an overall good image was obtained. The dampening form roller was disengaged (lifted up) and sheets were run through the press. The better fountain solution, with a minimum pH level of about 5.0 to 5.5. showed resistance to scum by running more sheets without any trace of scum on the The test was run twice with three replicates for press. The same test procedure was applied to gum arabic each run. The data and the analysis of variance are shown solution. in Table XVI and Table XVII. Results show that there is no significant statistical difference in resistance to scum of both solutions.

Table XV

Resistance to Scum of Both Solutions

	No. of) sh	leets	that	is	resistant	to scum
Fountain Solution	lst	Ru	in	2nd	Run		x
No. of Replicates	1	2	3	1	2	3	
Gum Arabic	8	13	11	7	9	14	10.33
Silicic Acid	13	19	16	11	8	17	14.00

Table XVI

ANOVA Summary Table for Resistance to Scum

Source	Sum of squares	Degrees of freedom	Mean square	F ratio
Treatment	16.34	1	16.34	0.828 N.S.
Type of solutions	40.34	5	8.068	0.409 N.S.
Interaction	8.32	0		
Error	98.67	5	19.734	
Total	163.67	11		
	Critical F	5, 5, 0.05 =	5.0503	
	Critical F	1, 5, 0.05 =	6.6079	
	N.S. No significa	nt statistica	l differ	ence

THE "BLINDING OF PLATE" TEST

Blinding occurs with excessive gum concentrations or by eventual gum deposition such as through precipitation by alcohol. The coated surface of the plate becomes less ink receptive and image gradually disappears. To test for blinding of plate, two identical plates were made. Each of the plates was mounted on the press at different times and testing solution was also put on the press. All the variables were controlled except that of the fountain solution. Sheets were fed through the press and samples were pulled. The better fountain solution with less acid did not blind the image on the plate. The test was run twice with two replicates for each run. The same test procedure was repeated with another testing solution on a new plate. Results:

The results of the experiments show that conventional gum arabic solution with a low contact angle did not blind the plate compared to silicic acid solution with a low contact angle. High concentration of sodium silicate blinds the plate in under 500 impressions. The data and analysis of variance are shown in Table XVIII and Table XIX. The calculated F ratio did not exceed the critical F ratio. This indicates that there is no significant statistical difference between the fountain solutions due to the ability to blind the plates.

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Blinding of Plate of Both Solutions

	No. of	sheets	until blind	ling	occurred
Fountain Solution	lst	Run	2nd	Run	X
No. of Replicates	1	2	l	2	
Gum Arabic	275	380	250	473	344.50
Silicic Acid	155	224	215	319	228.25

Table XVIII

ANOVA Summary Table for Blinding of Plate

Source	Sum of squares	Degrees of freedom	Mean square	F ratio
Treatment	6216.125	1	6216.125	0.4887 N.S.
Type of solutions	27028.125	3	9009.375	0.7082 N.S.
Interaction	949.125	0		
Error	38162.5	3	12720.83	
Total	72355.875	7		

Critical F_3 , 3, .05 = 9.2766 Critical F_1 , 3, .05 = 10.128 N.S. No statistical significant difference

THE "MINIMUM DAMPENING RATE TO CLEAN-UP THE PLATE" TEST

The most important function that a fountain solution fulfills is to keep the non-image areas clean by maintaining a continuous film of water over such areas. The better the formulation of the fountain solution, the less time it takes to clean up the plate after over-run with ink. Two identical plates were made for this test. The plates were mounted on the press at different times for each testing solution and the plates were allowed to desensitize. The dampening roller and ink rollers were in contact with the plate. Sheets were fed through until a solid density print was obtained. The dampening form roller was lifted up for 45 seconds. Sheets were fed through and samples were pulled. The dampening form roller was in contact with the plate: it cleaned up the plate. The test was run twice with three replicates for each run. Sheets were counted to show how many sheets were needed to obtain clean prints with minimum dampening solution. The same procedure was applied to the other fountain solution. Results:

The results of the experiments show that gum arabic solution took less number of printed sheets to clean up the plate after the plate was over-inked with minimum dampening solution compared to silicic acid solution. The data and analysis are shown in Table XX and Table XXI. The analysis indicates that there is no significant statistical difference between the two fountain solutions to clean the plates with minimum dampening rate.

Table XIX

The Minimum Dampening Rate to Clean-Up the Plates

Fountain Solution	No.	of sh	leets	to	obta	ain cl	Lean	prints
	ls	st Rur	1		2	2nd Ri	in	x
No. of Replicates	1	2	3		l	2	3	
Gum Arabic	15	18	12		19	21	16	16.833
Silicic Acid	19	23	25		21	26	20	22.333

Table XX

ANOVA Summary Table for Minimum Dampening Rate to Print Clean

Source	Sum of squares	Degrees of freedom	Mean square	F ratio
Treatment	10.09	l	10.09	0.7206 N.S.
Type of solutions	90.76	5	18.152	1.2964 N.S.
Interaction	10.06	0		
Error	70.01	5	14.002	
Total	180.92	11		

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Critical F_5 , 5, 0.05 = 5.0593 F_1 , 5, 0.05 = 6.6079

N.S. No significant statistical difference

THE "RATE OF DE-INKING OVER-RUN NON-IMAGE AREAS" TEST

For this test, two identical plates were processed and used. The plates were put on the press and allowed to dry. Then the plates were inked up solid by using fixed ink and water setting. The dampening form roller was dropped and sheets were fed through. The test was run twice with three replicates for each run. Sheets were counted to show how many sheets were needed to obtain prints that have certain low densities in non-image areas. The test procedure was applied to the other fountain solution.

Results:

Experimental results show that gum arabic solution took almost the same number of sheets to de-ink an over-run non-image area compared to the silicic acid solution. The data and analysis of variance are shown in Table XXII and Table XXIII. The calculated F ratio did not exceed the critical F ratio. This indicates that there is no significant statistical difference between the two fountain solutions because of the rate of de-inking over-run non-image areas.

Table XXI

Rate of De-Inking Over-Hun Non-Image Areas

	No.	of sl	heets	to obt	ain	low de	nsities
	over	– run	non-i	mage a	reas		
Fountain Solution	ls	t Ru	n		2 nd	Run	x
No. of Replicates	1	2	3	1	3	3	
Gum Arabic	20	18	23	19	16	21	19.5
Silicic Acid	31	26	29	23	27	28	27:33

Table XXII

ANOVA Summary Table for Ability of Solutions to Print Low Densities

Source	Sum of squares	Degrees of freedom	Mean square	F ratio
Treatment	14.09	l	14.09	1.3545 N.S.
Type of Solutions	183.74	5	37.748	3.6289 N.S.
Interaction	1.08	0		
Error	52.01	5	10.402	
Total	250.92	11		

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Critical F₅, 5, 0.05 = 5.0503 Critical F₁, 5, 0.05 = 6.6079 Calculated F ratio = $\frac{\text{Variance of Mean}}{\text{Variance of Error}}$

N.S. No significant statistical difference

PERFORMANCE DISTINCTION BETWEEN LITHIUM SILICATE AND SODIUM SILICATE TEST

Two different testing solutions, one containing lithium silicate and the other containing sodium silicate were made with the same pH number (5.0). Two identical plates were These plates were mounted on the press and inked up. made. Then the dampening form roller and ink rollers were dropped to be in contact with the plates. Sheets were fed through the press. The test was run twice for both high and low ink film thickness. The density was $1.50^{+}0.05$ for high ink film thickness and 1.20-0.05 for low ink film thickness. Twentyfive random samples were collected from each run for evaluation. Evaluation was carried out by measuring the printing sharpness of the tested solutions. Printing sharpness values are obtained by dividing the density of tint by the density of solid.

Results:

Observation shows sodium silicate to be a better constituent of silicic acid compared to lithium silicate. At .04 percent of lithium polysilicate solution in silicic acid, lithium silicate blinded the plate. It removed the lacquer on the image plate and re-lacquering could not build up the lost image. But lithium silicate did not gel-up as sodium silicate did in solution. They both deposited the same amount of solid ink density on the printed sheet.

The data are shown in Table XXIV through Table XXVI. Two factors with two replicates is used as an analysis of variance. Table XXVII summarized the ANOVA Table. The statistical results show that there is no significant difference in performance distinction caused by lithium silicate or sodium silicate of silicic acid solution at equal solid ink density. Figure 9 shows that the tone reproduction curve of both solutions are super imposed on each other.

Table XXIII

Printing Sharpness Values as a Measure of Performance Distinction of Lithium Silicate in

Silicic Acid Solution at Both High Ink Film Thickness $(1.50^{\pm}0.05)$ Density and Low Ink Film Thickness $(1.20^{\pm}0.05)$ Density

Sample of	High Ink	Film Th:	ickness Lov	Ink Film	Thickness
Printed Sheets	lst Run	2 n	i Run 1st	; Run	2nd Run
1	1.28	1.	28 1.2	27	1.21
2	1.27	1.	24 1.1	.9	1.07
3	1.11	1.	0.6	52	0.39
4 ·	1.12	1.	0.5	59	0.36
5	1.12	1.	09 0.5	55	0.38
6	1.10	1.	0.6	52	0.34
7	0.95	0.	93 0.7	78	0.58
8	0.94	0.	81 0.7	1	0.61
9	0.87	0.	75 0.6	57	0.50
10	0.91	0.	87 0.7	74	0.33
11	0.94	0.	93 0.6	52	0.37
12	0.85	0.	79 0.5	59	0.35
13	0.88	0.	73 0.7	71	0.40
14	0.89	0.	81 0.5	54	0.29
15	0.91	0.	71 0.5	50	0.35
16	0.88	0.	81 0.9	54	0.40
17	0.89	0.	66 0.5	58	0.44
18	0.82	0.	65 0.5	59	0.36
19	0.80	0.	72 0.0	51	0.50
20	1.23	1.	14 0.0	53	0.48
21	1.31	1.	26 0.0	64	0.34
22	1.28	l.	12 0.0	65	0.38
23	1.24	0.	90 0.'	70	0.43
24	1.21	0.	86 0.	73	0.41
25	1.30	1.	24 0.	69	0.39
Total	X = 26.10	X = 23.4	3	7.06 X =	11.66
	$\bar{k} = 1.044$	$\overline{X} = 0.93$	$\overline{X} = 0$.6824	0.4664

Printing Sharpness Values as a Measure of Performance Distinction of Sodium Silicate in Silicic Acid Solution at Both High Ink Film Thickness (1.50⁺0.05) Density and Low Ink Film Thickness (1.20⁺0.05) Density

Sample of	High Ink Film	Thickness	Low Ink Film	Thickness
Printed Sheet	lst Run	2nd Run	lst Run	2nd Run
1	1.25	1.21	0.69	0.39
2	1.26	1.25	0.65	0.36
3	1.19	1.15	0.63	0.37
4	1.23	1.22	0.64	0.35
5	1.24	1.20	0.64	0.34
6	1.21	1.20	0.71	0.34
7	1.27	1.24	0.60	0.38
8	1.31	1.14	0.66	0.38
9	1.24	1.20	0.69	0.40
10	1.24	1.22	0.69	0.40
11	1.25	1.15	0.68	0.35
12	1.22	1.13	0.78	0.37
13	1.23	1.16	0.65	0.35
14	1.10	1.04	0.69	0.37
15	1.12	0.85	0.67	0.36
16	1.17	1.04	0.64	0.36
17	1.14	0.94	0.56	0.35
18	1.17	0.91	0.59	0.36
19	1.13	0.88	0.63	0.38
20	1.13	0.98	0.65	0.33
21	1.11	0.93	0.69	0.39
22	1.14	0.85	0.64	0.40
23	1.17	0.91	0.73	0.32
24	1.22	1.02	0.61	0.32
25	1.13	0.97	0.63	0.36
Tota	1 X = 29.87 X	(= 26.79)	K = 16.44 X =	= 9.08
	X = 1.1948	$\bar{X} = 1.0716$	$\overline{X} = 0.6576 \overline{X}$	x = 0.3632

Performance Distinction Data From Lithium Silicate Solution and Sodium Silicate Solution at Both High and Low Ink Film Thickness

Fountain Solution	High Ink Film Thickness (1.5005) density solid	Low Ink Film Thickness (1.20 [±] .05) density tint
Lithium Silicate	26.10, 23.43	17.06, 11.66
Sodium Silicate	29.87, 26.79	16.44, 0.09

Table XXVI-A

ANOVA Summary Table for Performance Distinction

Source	Sum of squares	Degrees of freedom	Mean square	F ratio
Type of Solutions	1.9306	l	1.9306	
Solid Ink Density	42.8275	l	42.8275	0.4797 N.S.
Interaction	0.7023	1	0.7023	
Error	357.1318	4	89.2829	
Total	402.592	7		

Critical F_1 , 4, .05 = 7.7086

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N.S. No significant	statistical difference
Calculated F ratio =	Variance of Mean
Carcurated r latto -	Variance of Error

Performance Distinction Data From Lithium Silicate at Both High and Low Ink Film Thickness

Fountain Solution	High Ink Film Thickness (1.50-0.05) density solid	Low Ink Film Thickness (1.2005) density tint
Lithium Silicate	1.044, 0.9372	0.6824, 0.4664
Sodium Silicate	1.1948, 1.0716	0.0576, 0.3632

Table XXVI-B

ANOVA Summary Table for Performance Distinction

Source	Sum of squares	Degrees of freedom	Mean square	F ratio
Type of solutions	0.0030	1	0.0030	
Solid ink density	0.0685	l	0.0685	0.4794 N.S.
Interaction	0.0011	1	0.0011	
Error	0.5714	4	0.1429	
Total	0.644	7		

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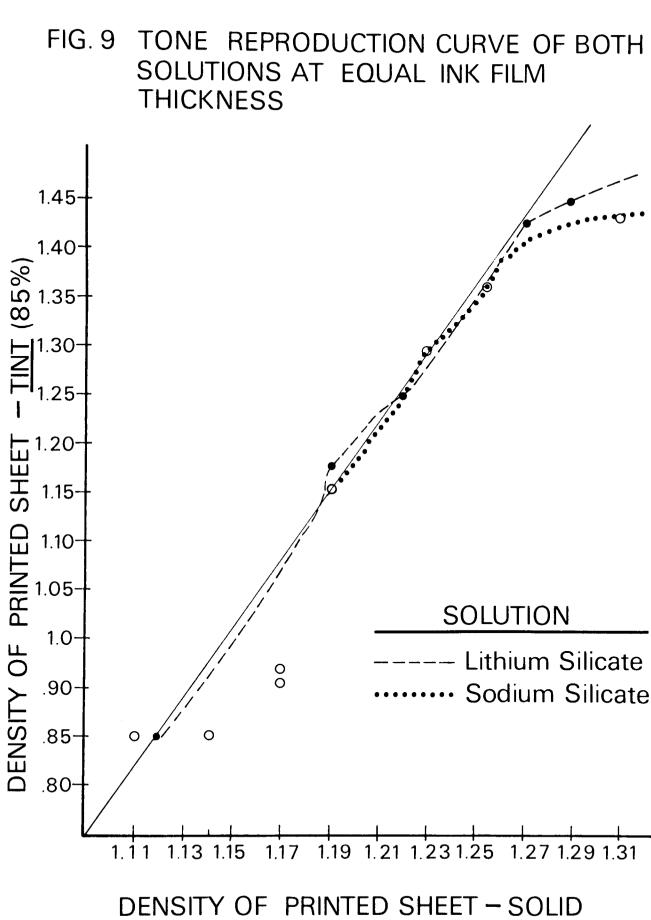
Critical F_1 , 4, 0.05 = 7.7086 N.S. No significant statistical difference Calculated F ratio = $\frac{Variance \ of \ Mean}{Variance \ of \ Error}$

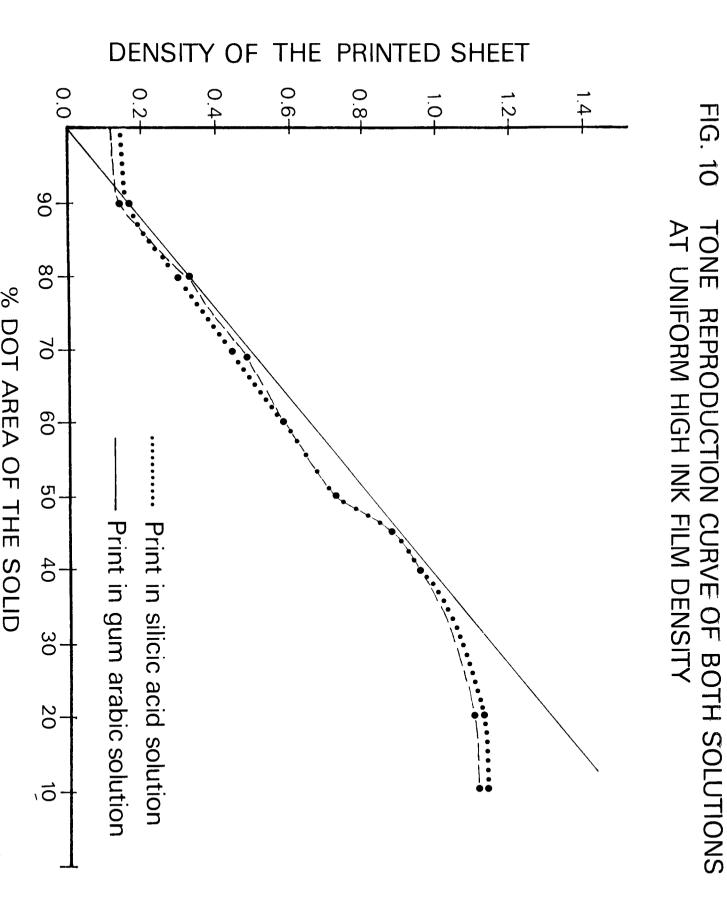
THE "CHANGES WITH AGING IN SOLUBILITY PROPERTIES OF SILICATES IN FOUNTAIN SOLUTIONS"

When silicates first form (hydrolysis of SiCl₄ with water), silicic acid appears in the form of simple molecules of low molecular weight. Because the molecular weight is said to increase very rapidly with time of aging, silicic acid polymerizes or the molecules aggregate to form layer groups.

The particles of the solution carry a negative charge in alkaline, neutral, and even in a weakly acid solution. In strongly acid solution the charge is positive, and is caused by ionization of silicic acid.

Changes with aging in solubility properties of silicates in fountain solutions would be attributed to the molecular weight, temperature, and concentration.





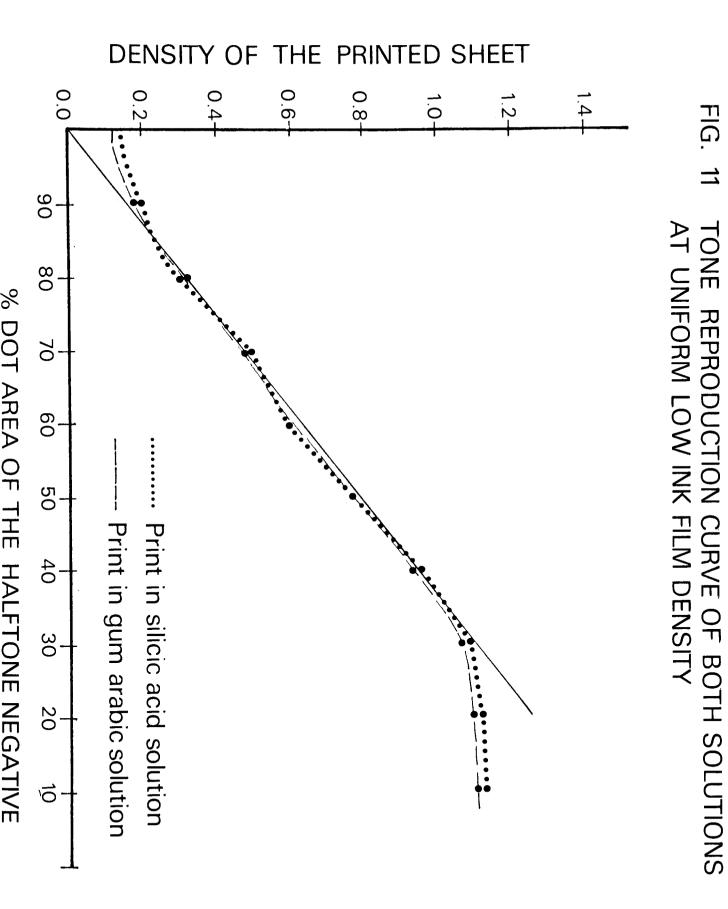


PLATE-PRESS CHARACTERISTIC CURVE

A tone reproduction study of a printing press may evaluate every phase of the printing system from the tones of the original print to the tones of the final reproduction.¹⁰ The relationship between the density of the printed sheet and the percent dot area of the halftone negative is termed the plate-press characteristic curve. This curve represents the gain or loss of the plate-press combination.

Figure 10 and Figure 11 show the plate-press characteristic curves obtained from two solutions. The percent dot area of each step of the halftone negative step tablet was plotted against the resulting densities of each step on the printed sheet. Under controlled conditions, the curves are alike and almost superimpose on each other.

Observation:

During the experiments, it was observed that silicic acid, when first introduced onto the press, causes the dampening roller to accept ink so that the whole press was inked solid. After the press was washed up, the press was run for 20 minutes.

When silicic acid was run on the press at high ink film thickness, it was observed that more ink was required to maintain a maximum solid ink density. Emulsification developed because of the foam-like character exhibited by silicic acid into the ink rollers. Tinting tended to develop.

The advantage of gum arabic solution over silicic acid solution is attributed to its non-gelling property. Although gum arabic is prone to bacteria attack within a few days after preparation, silicic acid has a high resistance to bacteria deterioration and thus deterioration of gum arabic during shelflife could give rise to high contact angle and therefore decrease the rate of wetting. This is one of the reasons that the effect of silicic acid in fountain solution is an important study. ¹"1974 Annual Book for ASTM Standards, Part 30," (Pennsylvania: American Society for Testing and Materials) p.206.

²R.A.C. Adams (P.A.T.R.A.) "Contact Angles and Their Significance in Lithographic Research," <u>International</u> <u>Bulletin</u> January 1956, p.20.

³Charles E. Martin, M. Sc. Thesis, "Image Dechanisms in Screenless Lithography," Rochester Institute of Technology, 1975.

⁴"Solutions to Sticky Problems," (Massachusetts: Brookfield Engineering Laboratories Inc.), p.9.

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Bruce E. Tory, Offset Lithography, (Horwitz Publications Inc., Pty. Ltd. 1957) Austria p.253.

⁶Albert D. Rickmers and Hollis N. Todd, <u>Statistics: An</u> Introduction (New York: McGraw-Hill Book Co., 1967), p.559.

⁷M.A. Bobb, M. Sc. Thesis, "Identification Thresholds of the Human Visual System for an Alphanumeric Resolution Test Object," Rochester Institute of Technology, 1975.

⁸Ibid.

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⁹Paul J. Hartsuch, Chemistry of Lithography (Pennsylvania: Graphic Arts Technical Foundation Inc., 1961) pp.305-306.

¹⁰Miles F. Southworth, "Objective Tone Reproduction in the Graphic Arts," Rochester Institute of Technology, 1974. (Typewritten)

CONCLUSIONS AND RECOMMENDATIONS

This study investigated the effectiveness of silicic acid as a constituent of fountain solution. The solution of this water soluble colloid was compared to the conventional gum arabic solution.

Investigations that were not carried out on the press included surface tension, wettability, and viscosity measurement of each solution at different concentrations and pH levels.

The surface tension was measured by the du Nouy Tensiometer Ring method. It showed that the surface tension of silicic acid is lower than that of gum arabic solution.

The wettability of a liquid on a solid surface was conveniently measured by the contact angle method. The contact angle obtained from silicic acid solution increased as the concentration increased while the contact angle of gum arabic solution decreased as the concentration increased.

The viscosity of both silicic acid and gum arabic solutions were measured by the Brookfield Synchro-Lectric Viscometer and showed differences. The viscosity of gum arabic solution increased as the concentration increased. But the viscosity of silicic acid solution decreased as the concentration increased. In this case, high viscosity with high concentration can be obtained by decreasing the rate of shear.

Investigations that were carried out on-press included the dot size change, the resolution, the resistance to scum, the blinding of plate, the minimum dampening rate to cleanup the plate, the rate of de-inking over-run non-image areas, the performance distinction between lithium silicate and sodium silicate and the changes with aging, in solubility properties of silicates in fountain solutions. The press performance was under controlled press conditions of plate, blanket, paper, and ink. The pH of the solutions were varied before a standard of about 5.0 was chosen as standard. The ink film thickness was also controlled. At high ink film thickness the optical density was $1.50^{\pm}0.5$ and at low ink film thickness it was $1.20^{\pm}.05$.

The different concentrations of silicic acid solutions needed were determined. Concentration ranged between 2cc to 25cc of silicic acid/100cc of water with a pH range of 3.5-7.0. The solution of gum arabic was determined with one ounce of 14 Baumé gum arabic and one ounce of 3M Fountain Concentrate to a gallon of water. Phosphoric acid and dilute hydrochloric acid were used to control the pH of the fountain solutions. The pH range was measured by the pH meter.

The method of data analysis used in this experiment is called analysis of variance (ANOVA). This method is an extension of the \underline{t} test of hypothesis for mean. Rickmers and Todd stated in their book that:

This method permits us to answer questions in a single test and with a single alpha risk. The kind of asked questions are: Do the data indicate that the members of a set of hypothesized population means differ among themselves? Are these differences significantly different from a chance result? The ANOVA is especially used when it is applied to complex situations.¹

The statistical analysis and observation indicated that there is no significant difference between the two solutions in terms of ability to maintain dot size on the plate, resistance to scum, resolution, ability to clean-up the plate, rate of de-inking over-run non-image areas, blinding of image on the plate. We then assume that silicic acid is comparable in effect in these regards except the dot size which was different because of concentration and gelling property. The ANOVA table shows significant statistical difference in the calculated value from the mean data but the interaction was not significant. The gum arabic gives a better dot size at both high and low ink film thickness. Gum arabic also gives resistance to blinding of the plate except when the pH is lowered to about 3.5. With silicic acid solution, a pH of 3.5 gave equal resolution and sharpness as a pH of 5.0 or higher but blinding occurs when the phosphoric acid that controls the pH could not bring the pH to a minimum level of acidity and if it is added in excess.

RECOMMENDATION FOR FURTHER STUDY

The experiment was carried out on one type of ink, paper, and plate. A study involving different types of inks, papers, and plates would be helpful in determining the kinds of materials necessary to be used with this desensitizer.

It would be interesting to study the effect of phosphoric acid used in varying the pH levels with regard to gelling of silicic acid. It would be interesting to study the incompatability of alcohol in silicic acid solution which may contribute to plate blinding because colloids tend to migrate to interfaces.

Chromic acid combines with silicic acid to form a soluble complex, thus lowering the concentration of polymerizable silica in the system.² It would be of value if chromic acid effect can be investigated with respect to polymerization.

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FOOTNOTES FOR CHAPTER TV

¹Albert D. Rickmers and Hollis N. Todd, <u>Statistics:</u> <u>An Introduction</u> (New York: McGraw-Hill Book Co., 1967), p.175.

² Ralph K. Iler, "The Colloid Chemistry of Silica and Silicates," Polymerization, Cornell University Press, Ithaca, New York: p.55 (1955).

APPENDICES

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APPENDIX A

CONTROLLED VARIABLES AND TEST OBJECTS (CONDITIONS):

1. Plate: 3M presensitized, negative working aluminum plate, type "Qc." The exposure time was $l\frac{1}{2}$ minutes and developed to the critical solid step No.6 of the GATF Sensitivity Guide (as recommended by the manufacturer). The plate was prelacquered and used for a medium run.

The reasons for using this plate are: (a) A pre-lacquered plate will avoid the problem of image sharpening due to the prolonged use and ink changes. (b) Minimize plate problems such as fill-in or piling when lacquering.

2. Ink: Litho Van Son Inks, GPI Split - Sec. No.40904 for uncoated stock. Net wt. 13 oz., and it is neutral black.

3. Paper: Consolidated "White Paloma Matt, blade coated" dull finish, 60 lbs., $8\frac{1}{2}$ xll." This stock was used because of availability, prevention of set-off and the surface was suited for the kind of test that was planned.

4. pH of fountain solution: Standard - between 4.5 - 5.0 as recommended by GATF. pH levels were measured by pH meter.

5. Press: 1250 Multilith was used for all experiments. The conditions such as plate to blanket pressure, back cylinder pressure, inking unit and dampening unit were adjusted as recommended by the manufacturer. The back cylinder pressure was adjusted to the minimum pressure and good transfer of the ink image from blanket to paper was obtained.

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The press speed was 4,500 impression per hour (IPH). The blanket was a compressible type, "Vulcan 714," manufactured by Reeves Bros., Inc. Dampening form roller: paper type, 3M brand dampening sleeve. 6. Press sheets showing the test objects (patterns) which were printed are shown in Appendix E.

These include the following:

(a) Printing sharpness objects are made up of nine solid patches in line across the sheet and nine halftone patches of the same size. The halftones were printed under the solid. The halftones are 133-150 lines, 45,75,105,90 percent tints. The solid patches were used as control bars for controlling density across the sheet. The correlation of solid ink density (SID) to tint density is the sharpness value.

(b) GATF Stouffer sensitivity guide, a 21-steps of continuous tone gray scale. This guide was used to give a uniform scale of light transmission for measuring plate exposure.

(c) The standard RIT ALPHANUMERIC RESOLUTION TEST OBJECTS was used for the evaluation of resolutions of line-work, halftone and resolution change variables.

(d) The slur target or test object consists of letters "M" and "A". They are made up of 10 and 85 percent tints. The slur test object is a test image designed to show variations in the amount of slur along and across the press sheet.

(e) The halftone pictures of 150,133,120,110, line were used for the evaluation of dot size change. Plate-press curves were generated. The plate-press curve is useful for evaluating the distortion caused by a given plate-press combination. The response variable is the percent dot area of film used to make the plates. The effective dot area on the printed sheet was calculated by using the Yule-Neilsen equation. The comparison of dot size changes was made on 150 and 110 line screens.

APPENDIX B

WETTABILITY OF THE NON-PRINTING AREAS

When a drop of liquid is placed on a solid, it sometimes spreads out immediately to cover the entire surface of the solid, but usually it remains in the form of a lens.

Wettability is the behavior of a liquid and a solid when the liquid is trying to spread on the solid. The degree of wetting can be described numerically by the magnitude of the three interfacial tensions:¹

- 1. The liquid/solid
- 2. The liquid/air and
- 3. The solid/air.

Thus the criterion for wetting is whether the solid/air interfacial tension is greater than that for solid/liquid or not. If it does, the liquid will wet the solid and the contact angle will be less than 90 degrees. If it does not, the liquid will not wet the solid and the contact angle will be greater than 90 degrees.

The behavior of a liquid on a solid surface is characterized by a quantity called the contact angle.² A contact angle of zero implies complete wetting of the solid surface by the liquid, while a value of 180° would correspond to absolute non-wetting. In the offset-lithographic printing, the non-image areas should show contact angles approaching zero towards water while the image areas should show a contact angle approaching 180° .

The factors that mostly affect the water-receptivity of non-image areas are: 3

- 1. The metal themselves
- 2. The surface treatments given the metal
- 3. The desensitizing process
- 4. The fountain solution with which the plate is run, and
- 5. The gumming.

Metals such as chromium, aluminum, and stainless steel form hard, tenacious oxides which are easily wet by water and retain their wettability for a long time. Zinc or iron is not wet as readily by water because zinc forms loose corrosion products similar to rust. The wettability of metals changes as they undergo different stages of corrosion.

The ability of a metal to be wet with water is enhanced by the application of a solution of a gum. How well the gum or etch sticks to the metal depends on the composition of the etch and the condition of the metal; if a foreign material is adsorbed to its surface, the gum will not stick. Thus, the surface treatment is needed to eliminate difficulties caused by these defects and to improve the wettability of metals.

A surface-treated metal does not corrode, does not react with coating, and is not affected by the solutions used in the lithographic process; coating and gum stick well to the treated metal.

The purpose of an etch is to deposit a water-receptive material on the non-image areas of the plate. A good etch should leave a droplet or film of water-receptive material which lasts for a long time on the press, and wet with a minimum of water.

An etch usually consists of gum, an acid, and one or more salts. The main ingredient of the etch is the gum, often gum arabic. Gum arabic contains carboxyl groups which give a firm bonding between the gum and the metal. The gum swells when water is present, but the carboxyl bond keeps the gum from dissolving away from the metal.

Phosphoric acid is used to convert more of the groups in the gum molecule into carboxyl groups to improve the adhesion. Too much acid attacks the metal which, in this application, instead of forming a droplet or film on the metal, removes metal. ¹R.R. Coupe, <u>Science of Printing Technology</u>, (London: Cassell and Company Ltd., 1966), pp.73-74.

²R.A.C. Adams, "Contact Angles and Their Significance in Lithographic Research," <u>International Bulletin for the</u> <u>Printing Allied Trades 73</u>. (January 1956), p.20.

³Charles Shapiro, ed., <u>The Lithographers Manual</u>, (Pennsylvania: Graphic Arts <u>Technical Foundation Inc.</u>, 1974), pp.10: 17-10: 18.

APPENDIX C

SURFACE TENSION

Young¹ gave a vivid explanation of the surface tension in terms of the attractive and repulsive forces between the molecules constituting the liquid. Young stated that:

> The cohesion between the molecules of a liquid must surpass their tendency to separate under the influence of thermal motion.²

In the body of liquid, a molecule is attracted equally in all directions while a molecule at the surface is subjected to an unbalanced forces that acts inwards to the surface.

The force, acting perpendicular to a centimeter length of surface, and in the surface is called the surface tension. It is expressed in dyne per centimeters.

Surface tension can be measured quantitatively by various means,³ including the pulling of a wire ring from the surface of a liquid, the weighing of drops which fall from a special glass tip, the determination of the shape of a liquid, and the pressure required to blow gas bubbles in the liquid.

There is every possibility of running a plate with only plain water if the plate has been well desensitized, but water has a high surface tension. If water is used alone, it will require greater amounts for dampening the plate. Therefore, some wetting agents, such as gum arabic, cellulose gum, alcohol, etc. are added to reduce the surface tension of water and cause the liquid to readily wet a solid surface.

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¹J.T. Davies and E.K. Rideal, <u>Interfacial</u> <u>Phenomena</u>, (London: Academic Press Inc., 1963), p.1.

²Ibid.

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³Farrington Daniels, <u>Outlines</u> of <u>Physical</u> <u>Chemistry</u>, (New York: John Wiley and <u>Sons Inc.</u>, 1948), pp.184-186. 1.

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One of the principal factors that control the chemical reaction of fountain solutions is the pH of the solution. The pH value of a solution is a number used to express the concentration of ionized hydrogen (the acid part) in a dissociated liquid, and is however, a measure of the immediate acidity or alkalinity.¹

As the hydrogen ion concentration increases, the pH of the solution decreases and the greater the acidity of the solution, the lower the pH value. The pH scale runs from 0 to 14. The middle points, 7, indicates a neutral solution while the values above 7 are alkaline, and below 7 are acid.

Two methods are used for measuring the pH of a solution, they are: (1) The colorimetric method and (2) the electrometric method. 2

The colorimetric method depends on the change of color of materials called indicators which are added to the solution. Indicators change color over a range of about two pH units. Different indicators must be used for accurate measurement over the scale. Paper strips for the colorimetric measurement of pH are also available, such as the "pHydrion pH paper."

The electrometric method depends on the change of the voltage of a little electrical cell, as the pH of the solutions of the electrical cell changes. The cell is calibrated by measuring the voltage when the cell is filled with a solution of known pH. By knowing that the voltage of such cells change, it is possible to calculate the pH of any unknown solution. In practice, the meters have been calibrated to read directly in pH units.

The fountain solution is usually acidic. The proper amount of phosphoric acid and hydrochloric acid are used in the solution to improve the adherence of the desensitizing gum to the non-image area. The acids convert the desensitizing gum to its "free acid form" in which the molecules contain corboxyl groups (-COOH). These groups are able to form a good adsorption bond of gum to the metal surface.³ If an excess amount of acid is added to the fountain solution, it will remain in the solution as a free phosphoric acid and begin to react with the metal of the plate. The plate loses its desensitization and ink adheres to the non-image area causing scumming or catch-up. Plate blinding and roller stripping may occur in conjunction with plate catch-up. Also, inks with a strongly emulsified acid fountain solution take a longer time to dry.

However, the correct amount of acid in the fountain solution depends on materials being used such as ink ingredients, plate treatments, and pH of paper. As recommended by the GATF, usually a fountain solution with a pH between 4.0 and 5.0 is satisfactory. It is suggested that the pH of the solution be thoroughly checked when printing trouble develops.⁴ The reason is that a fountain solution may change in pH on the press, during the press operation. ¹Bruce E. Tory, <u>Offset Lithography</u>, (Australia: Korwitz Publications Inc., 1957), p.82.

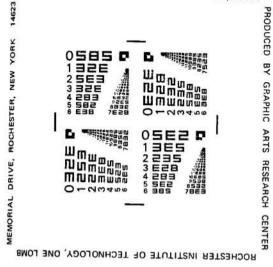
²Paul J. Hartsuch, <u>Chemistry</u> of <u>Lithography</u>, (Pennsylvania: G.A.T.F. Inc., 1961), p.51.

³Ibid., pp.53-56.

⁴Charles Shapiro, ed., <u>The</u> <u>Lithographers</u> <u>Manual</u>, (Pennsylvania: G.A.T.F. Inc., 1974), p.12:47.



RIT ALPHANUMERIC RESOLUTION TEST OBJECT, RT-1-71



CROWELL MACHINE SAW COMPANY

Scoreboard

Soccer Team Still Winless

The RIT soccer team played their first ICAC-conference game last week hosting Alfred Tech but fell to defeat in one of the Tigers' best games of the season.

Those who watched saw Alfred take a 2-0 lead early in the first half. The two goal lead seemed to put some fire into the Tigers' offense as they fought back to tie the game before the first half and take the punch out of Alfred's defense. Scoring the goals were Jim Page and freshman Per Haack Kjeldsen, a student from Denmark, putting in his first goal for the RIT squad. There were times in that first half that should have put the Tigers ahead but a weak left side saw those chances fail.



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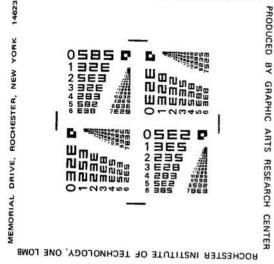
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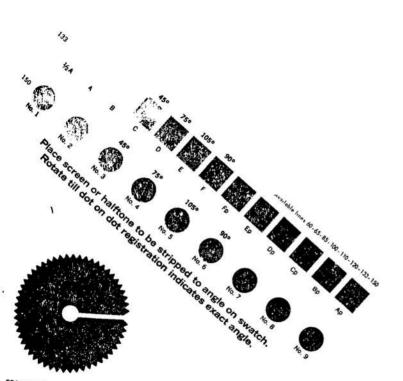
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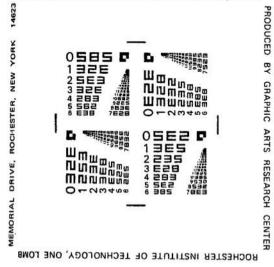
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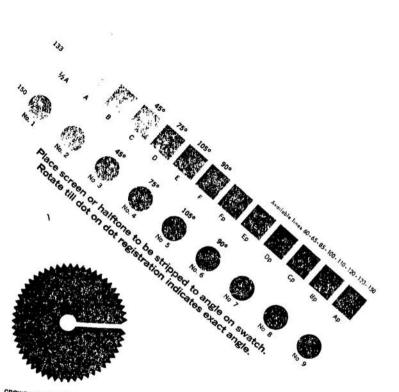
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TRIANGLE FASTENER COMPANY

RIT ALPHANUMERIC RESOLUTION TEST OBJECT, RT-1-71





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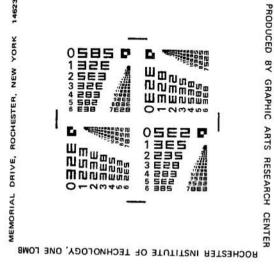
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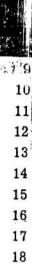
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Silicic Acid

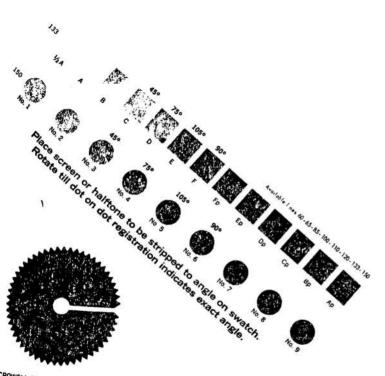


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RIT ALPHANUMERIC RESOLUTION TEST OBJECT, RT-1-71

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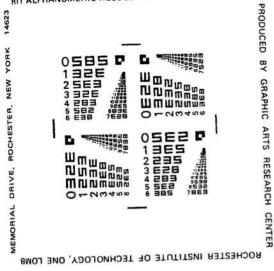






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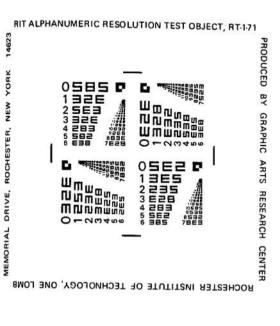
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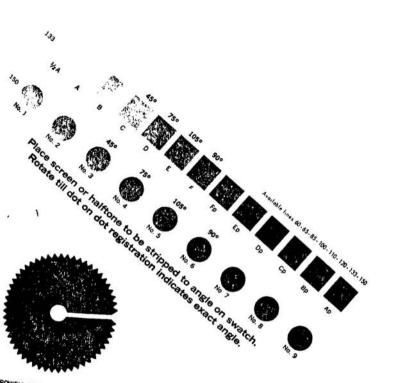
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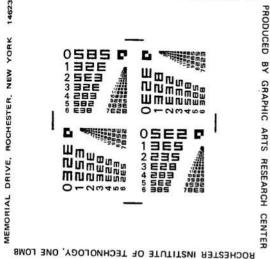
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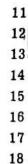
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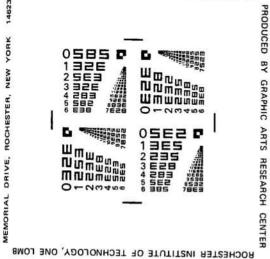
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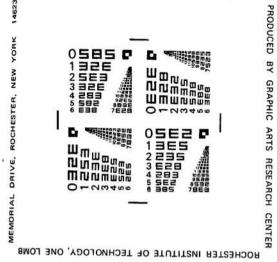
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