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THE PROBLEM OF GELLING WHEN SILICATES ARE SUBSTITUTED FOR GUM ARABIC IN LITHOGRAPHIC FOUNTAIN SOLUTIONS

by

David Wang

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

April 1984

Thesis Advisor: Dr. Julius L. Silver

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ABSTRACT

The fountain solutions used for lithographic offset printing are solutions combining several chemicals. Each consists of water, some weak acid, gum arabic and alcohol in some fountain solutions, and some additives such as a nitrate, phosphate, bichromate, etc. This paper is a study of using polysilicate material instead of gum arabic in lithographic fountain solutions. Also, to solve the problem of silicate gelation by using the proper ratio of chemicals.

The gelling problem of silicate material may be affected by the concentration, pH value, organic solvents and impurities, etc. Any one of the above will make the silicate material gel faster or retard the gelation. Hence, the kind of chemicals used are very important to the properties of polysilicate fountain solutions. The amount of those chemicals in the polysilicate fountain solution is also important for the gelling time.

By controlling the ratio of chemicals, the gelling problem was solved with retarding of gelation. A pilot test, run by using a non-linear programming package, was done before the experimentation. The gelling time was prolonged long enough for lithographic fountain solution use.

A series of press tests was accomplished with a Chief 15 duplicator to affirm the possible usage of polysilicate fountain solutions. The press tests also proved the gelling problem does not exist on the running press.

After using the ratio of chemicals found in this paper, the polysilicate fountain solution can be practically in use.

Abstract approved:__________________, thesis advisor

__________________, title and department

__________________, date

CHAPTER I

INTRODUCTION

The purpose of this study is to determine whether silicates can be used in place of gum arabic in lithographic fountain solutions. Gum arabic readily spoils by bacterial action and also may create problems of accumulating in bearings and gears of the press and of drying on the plates to cause gum blinding. Previous studies have shown that promising substitutes for gum arabic cause unacceptable increases in the viscosity of fountain solutions. This problem also is present in the case of silicates. This study investigates the possibility of developing low viscosity fountain solutions containing silicates without a decline in effectiveness as a fountain solution.

Fountain Solutions of the Lithographic Process

Two kinds of fountain solution may be used in the lithographic field, (A) the conventional fountain solution and (B) the alcohol fountain solution.

(A) Conventional fountain solutions.

This kind of fountain solution usually contains water, gum arabic and some additives such as nitrate, phosphate and bichromate salts and phosphoric acid (H_3PO_4). Some also contain calcium fluoride, chromic sulfate, chrome alum, tannic acid, glycerine, nickel salts, etc.[1] They usually do not include any alcohol.

(B) Alcohol fountain solutions.

Because of better wettability, some people add alcohol to fountain solutions to reduce the surface tension. All the fountain solutions with alcohol included are called alcohol fountain solutions. The fountain solutions can be as high as 50 percent alcohol without any harmful effects.[2] In using alcohol (e.g. isopropanol), the alcohol fountain solution usually is up to 30 percent alcohol at most.[3]

(1) Background of alcohol fountain solutions.

In 1952, Martinson recommended the use of alcohols as an additive in fountain solutions to help wet and spread the fountain solution over the ink in the article entitled, "The Use of Low Molecular Weight Alcohol in Lithographic Fountain Solutions." The Dahlgren dampener system patented in 1965 was responsible for its widespread use.

The theoretical background of alcohol fountain solution is related to surface chemistry which holds that high energy liquids will not spontaneously wet or spread on low energy surfaces. Low energy liquids can wet and spread on high energy material. In addition, Schalapfer[4] states that any contact between ink and water in lithography involves the ink film taking up water either on the surface or in the bulk. Surface tension and interfacial tension values govern only whether the water will spread on the ink film after splitting at the nip exits, not whether ink will take up water. This infers some degree of emulsification between ink and water solution (fountain solution). But emulsification will never happen spontaneously unless a significant amount of mechanical energy is applied to the components. So, it is not surprising to find water layers at the surfaces of ink rollers and inked areas of the plates even when using high surface tension fountain solutions that are not supposed to spread on to the low energy ink surfaces.

Thus, if the fountain solution has lower surface energy (lower surface tension), it will wet the ink more easily than the conventional fountain solution. Isopropanol has been introduced as a water-soluble material which has low surface energy and evaporates easily. It can be one of the additives in fountain solutions to lower the surface tension. Therefore, a fountain solution containing alcohol can easily wet ink surfaces and easily spread across ink surfaces to improve the wettability of lithographic plates.

(C) The property of gum arabic in lithographic fountain solutions.

Gum arabic (gum acacia) is the oldest and best known of the natural gums. Chemically it consists of the mixed magnesium (Mg) and calcium (Ca) salts of a complex polymeric hydroxy acid with a molecular weight around 240,000 -

300,000. The exact structure of gum arabic is not known, but it exists in nature as a neutral or slight acidic salt of a complex polysaccharide.

> A proposed tentative structure for gum arabic suggests a main chain of D-galactopyranose units linked $C_1 \rightarrow C_3$, with branched chains on C_6 consisting of D-galactopyranose, D-glucuronic acid, and L-arabofuranose. Some additional side branches of L-rhamnopyranose are also present on the D-galactopyranose side chains (25).[5]
>
> Gum arabic solutions are slightly acidic with a pH of 4.5 - 5.5. The maximum viscosity of the gum solution is at pH6-7 and is lowered by the addition of electrolytes, protracted heating, or long exposure to acid conditions which may cause partial hydrolysis.
>
> Gum arabic is insoluble in alcohol and other organic solvents. It is slightly soluble in aqueous alcohol, with the solubility decreasing as the proportion of alcohol to water increases up to about 60% alcohol, at which level it is practically insoluble.[6]

But gum arabic is highly hydrated in aqueous solution. It behaves in its aqueous solution as a typical colloidal electrolyte and the free acid (arabic acid) can be identically seen by the affect of the presence of foreign electrolytes. The free acid has an equivalent weight of about 1250.[7]

CHAPTER II

THEORETICAL BASES AND LITERATURE REVIEW OF SILICATE FOUNTAIN SOLUTIONS

The Soluble Silicates

The fountain solutions' additives in the lithographic process must have the ability to dissolve in water. Those silicates which dissolve in water are possible gum arabic substitutes since soluble silicates are very hydrophilic materials. R.A.C. Adams'[8] paper was on the comparison of the relative lithographic desensitizing strengths of some water-soluble materials. Although silicates were not used, the paper found the most efficient desensitizer at that time was polygluconic acid while monomeric d-gluconic acid was itself a good desensitizer with a limiting minimum concentration (L.M.C.) of 0.05 and higher than alginic acid (L.M.C. between 0.004 and 0.007). Thus it appears that with a monomer, which is a desensitizing material, polymerization can increase its effectiveness. Comparing with several of the natural high polymers containing both hydroxyl and carboxyl groups, it can be seen that in general the lower the equivalent weight, the greater the efficiency.

(A) Formation of polysilicate ions in aqueous solution.

The overall conversion of silica to silicate may be represented as follows:

$$(SiO_2)_{solid} + 2H_2O \longrightarrow Si(OH)_4$$

$$Si(OH)_4 + H_2O + OH^- \longrightarrow (H_2O)Si(OH)_5^-$$

$$(H_2O)Si(OH)_5^- + OH^- \longrightarrow Si(OH)_6^= + H_2O$$

It will be noted that the above formula indicates that silicon in the silicate ions is considered to have a coordination number of 6. For most purposes, the formula might as well be written in the more conventional manner in which silicon is represented as having a coordination of 4.

$$(SiO_2)_{solid} + 2H_2O \longrightarrow Si(OH)_4$$

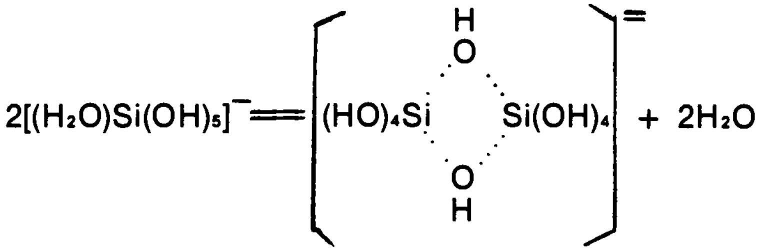
$$Si(OH)_4 + OH^- \longrightarrow (HSiO_3)^- + 2H_2O$$

$$(HSiO_3)^- + OH^- \longrightarrow (SiO_4)^= + H_2O$$

However, W.A. Weyl pointed out that there are advantages in considering the silicon atom to have a coordination number of 6 in alkaline solutions, since it is easier to visualize the probable mechanism by which polymerization of silica occurs.

Weyl prefers the following formulation and indeed visualized silica gel as made up of a polymer of $Si(OH)_4$ in which each unit is coordinated with the next in a linear polymer.

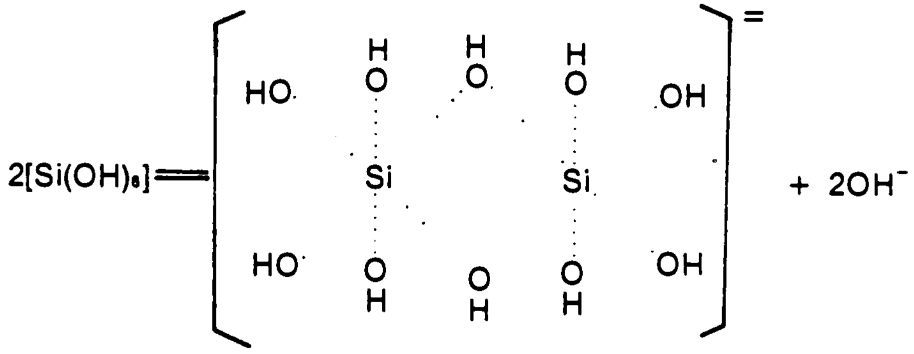
$$[Si(OH)_6]^= + H_2O \rightleftharpoons [(H_2O)Si(OH)_5]^- + OH^-$$



An alternative representation is:

$$2[(H_2O)Si(OH)_5]^- = [(H_2O)(OH)_4SiOSi(OH)_4(H_2O)]^= + H_2O$$

In terms of a coordination number of 6, the mechanism for forming the polymer:



Higher polymers may then be formed:

$$[Si(OH)_5 \cdot [Si(OH)_4]_n \cdot Si(OH)_5]^= + Si(OH)_6^= = [Si(OH)_5 \cdot [Si(OH)_4]_{n+1} \cdot Si(OH)_5]^= + 2OH^-$$

However, the evidence does not prove that the central $Si(OH)_4$ unit can retain a coordination number of 6. The formation of discrete particles favors the idea that the neutral units condense to the form of SiO_2 with a coordination number of 4.

> In view of the tendency of SiO_2 to form amorphous structures, it is probable that the polysilicate ions in sodium silicate do not have the highly ordered structure which is characteristic of the typical 'isopolyacids.' The higher molecular weight polysilicate ions may nevertheless be found to resemble heteropoly-acid anions in that there may be a spherical arrangement in which the charges will be borne by groups containing 6-coordinated silicon atoms on the surface of a spherical

> polyanion, while the neutral SiO_2 will be within the interior of the polyion and will contain silicon with a coordination number of 4.9

The step leading to the formation of the tetrahedrally coordinated SiO_2 from a polysilicate ion corresponds to the reaction:

$$(H_2O)Si(OH)_5^- \rightleftharpoons Si(OH)_4 + OH^- + H_2O$$

and may also be:

$$HSiO_3^- + H^+ \rightleftharpoons H_2SiO_3$$

If H_2SiO_3 (or $Si(OH)_4$) is stable in aqueous solution, the disilicate ions form when two parts of $HSiO_3^-$ with one part of H_2O, convert to the free non-ionized acid if the pH is lowered to 7.5 at 1.0 molar silicate solution.

The polysilicic acid, formed when acid is added to soluble silicate, is depolymerized by alkali. However, alkali does not reverse the type of polymerization brought about by salts in an alkaline silicate solution. In the salt-induced polymerization, salts increase in effectiveness in the order lithium, potassium, sodium. "The rate of polymerization is proportional to the fourth power of the concentration of added salt and inversely proportional to the square root of the silicate concentration."[10]

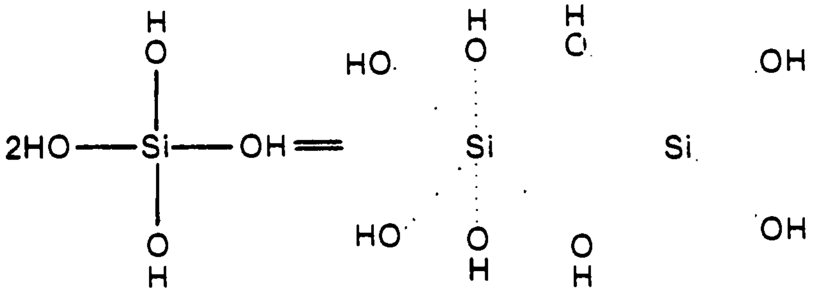
(B) Polymerization of silicic acid.

The overall equation for the polymerization may be written as follows:

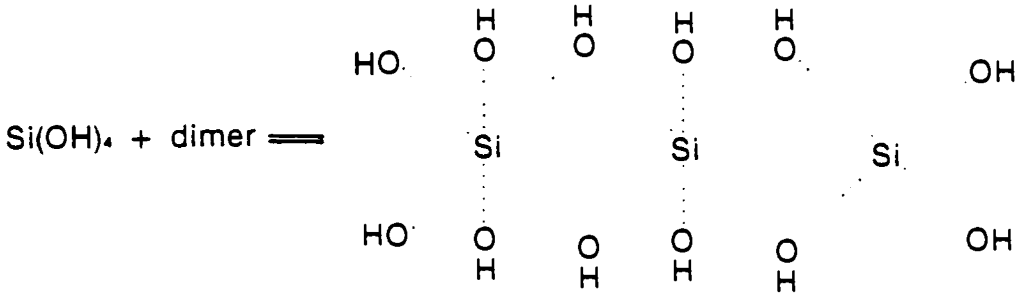
$$n\mathrm{Si(OH)_4} = (\mathrm{SiO_2})_n + 2n\mathrm{H_2O}$$

W.A. Weyl[8] has developed a hypothesis that silicon may have a coordination number of 6 with respect to oxygen in the form of OH groups. According to the equation above, the polymerization involves the condensation of silanol (Si(OH)) groups to form siloxane (Si - O - Si) bonds.

So that the reaction may be represented as follows, as water is eliminated:[8]



(dimer)



(trimer)

(C) Polymerization of silicic acid in acidic vs. basic solution.[11]

Kruyt and Postma pointed out that there are two groups of silicic acid sols. The first group has a pH of 4.5 or less, and the viscosity of the sol increases with time. On the other hand, pure silica sols, having a pH of 7 or higher, are relatively stable, the viscosity either remaining the same or decreasing with time ... . The more alkaline sols bear a negative charge and are thereby stabilized. However, the addition of soluble salts lowers the charge of the particles and causes gelation or flocculation. On the acid side, where there is essentially no charge, aggregation or flocculation occurs, causing an increase in viscosity and eventually gelation. ... in acid solution, fibrillar or network structures arise through the formation of oxygen bridges between silicic acid units. ... the "active" silica is obtained by partially neutralizing a dilute solution of sodium silicate with acid and is patented by Alexander, Iler and Walter. Because of the coagulating effect of the sodium salts in the solution, the concentration of the reactants must be kept low if aggregation or gelling of the sol is to be avoided.[11]

(D) Factors affecting polymerization of silicic acid to form gels.

(1) Factor of pH value.

The general relationship between pH and stability of silicic acid on colloidal silica with regard to gelling is shown in Figure 1.[12]

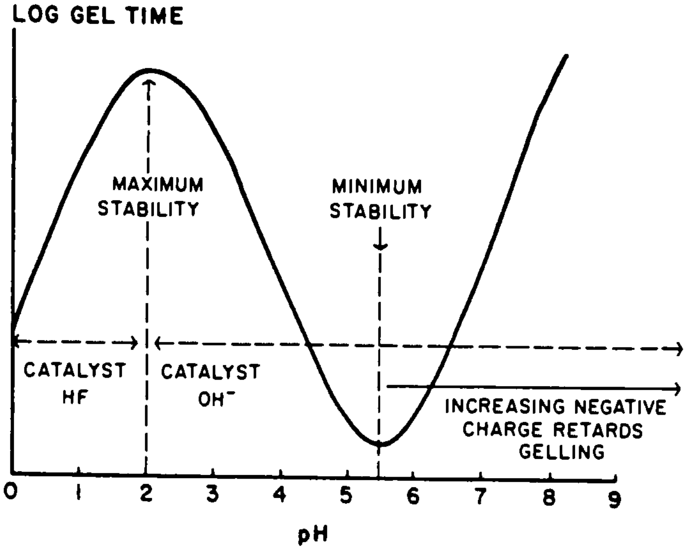


Figure 1. - Sol stability: relation between log (gel time) vs. pH

In this figure from about pH2 to 5 the charge on silica or silicic acid is low, so that presumably the molecules can easily collide. However, in this region, the OH^- groups is a catalyst of the condensation reaction. Also, according to the figure, the rate in the region below pH2 is proportional to the concentration of H^+ groups and the catalyst in this region, being a function of H^+ groups and F^- groups.

Between pH2 to 3, the polymerization is least rapid in aqueous solution; also the solutions of polysilicic acid increase in molecular weight most slowly and gel most slowly. The reason for the minimum rate of polymerization of silicic acid at around pH1 to 3 has been discovered by Iler.[13] At the lower pH, the polymerization is catalyzed by hydrogen fluoride (proportional to the concentrations of hydrogen ions and fluoride ions). As little as 0.1 milimole of fluoride per liter has a marked effect.[14] The observation that silicic acid is ordinarily found to be most stable within the pH range from 1.0 to 3.0 depends upon the purity of the solution. The pH of optimum stability may change.

Below about pH5, the rate of reaction between polysilicic acid molecules is proportional to (1) the number of collisions and (2) the concentration of OH^- ions which catalyze the reaction when collision occurs. However, above pH4.5, the polysilicic acid molecules become negatively charged. The rate of gel formation decreases as the pH is increased past the point where the decreasing number of collisions offsets the increasing concentration of the OH^- ion catalyst.

(2) Factor of concentration.

The solutions of silicic acid gel more rapidly with increasing concentration of silica, if the other conditions remain the same. Merrill and Spencer,[15] reported that at constant temperature and pH value ($pH \fallingdotseq 4.8$ to 6.5), the gel time was inversely proportional to the square of the silica concentration.

The retarding effect of chromate ion on the rate of gelation, investigated by Iler, is probably due to its effect on the concentration of free silicic acid in the system. In this case, it is postulated that chromic acid combines with silicic acid to form a soluble complex, thus lowering the concentration of polymerizable silica in the system.[16]

(3) Factor of organic solvents.

At pH below about 4.0 alcohols, ketones and ureas tend to stabilize polysilicic acid by hydrogen bonding. Above this pH, the addition of organic solvent lowers the dielectric constant of the solvent medium. This can lower the effective charge on the silica and promotes flocculation or gelling which is described by Baxter and Bryant.[17]

(4) Factor of impurity.

As said before, the presence of fluoride ion in the reagents reduces the gelling time. The aluminum or iron impurity may have a marked effect on the acidity of silicic acid, since aluminosilicic acid is a stronger acid than silicic acid. So, the pH value will be lowered by mixing with those metal ions.

(E) The reactions of polysilicic acid.

The reactions of polysilicic acid have not been widely studies because of the complexity of the reactions. But the observation that the precipitation of polysilicic acid by gelatin was inhibited by hydrogen-bonding agents offered a convenient point to begin experimentation. After some experimentations, the data which were obtained showed that when other factors were held constant, precipitation occurred as the concentration of salt exceeded a critical value. On the other hand, with the concentration of salt held constant, solubilization of the precipitate occurred (or precipitation was inhibited) when the concentration of the hydrogen-bonding agent exceeded a certain critical level. The coagulating effect of electrolyte was therefore offset by the solubilizing effect of the hydrogen-bonding agent on the gelatin-silicic acid complex.[18]

The Application of Polysilicate Fountain Solution in the Lithographic Process

In this paper, lithium polysilicate, isopropyl alcohol and phosphoric acid have been selected as components in polysilicate fountain solutions. Each chemical used is discussed as follows:

(A) Lithium polysilicate.

The reason for the choice of "lithium" polysilicate is because when acid is added to the polysilicate it forms the metal ion and polysilicic acid. As said before, the lithium cation with the acid anion in the fountain solution is equal to lithium salt being put into the solution. This action will cause the polymerization of polysilicic acid which coagulates. Since salts increase in effectiveness in the order of lithium, potassium, sodium, it is preferred to use "lithium" silicate. Also, because the monomer's desensitizing effectiveness is increased by polymerization, using polysilicate instead of silicate will increase the molecular weight of polysilicic acid.

(B) Denatural alcohol.

One needs a good hydrogen-bonding agent to prevent silicate gelling. It should have good solubility in water and not be toxic, and not have a bad odor. Alcohol is a good choice. Table I[19] shows the relative effectiveness of hydrogen-bonding agents.

TABLE I

Relative Effectiveness of Hydrogen-Bonding Agents

	Compounds	Relative Molar Effectiveness
(Standard)	Dimethoxytetraethylene glycol	100
Alcohols	Methanol	3
	Ethanol	6
	Isopropyl alcohol	11
	t-Butyl alcohol	16
Glycols	Ethylene glycol	0
	Propylene glycol	7
	3-Methyl-1,2-butanediol	18
	Hexamethylene glycol	27
Ketones	Acetone	17
	Methyl ethyl ketone	25
Amides	Formamide	0
	N,N-Dimethylformamide	25
	N,N-Diethylformamide	10
	Acetamide	11
	N,N-Dimethylacetamide	41
	N,N-Diethylacetamide	54
	N-Isobutylacetamide	22
	Urea	7
	Tetramethylurea	44
Primary Amines (as salts)	Methylamine	0
	Cyclohexylamine	25
	2-Ethylhexylamine	32
	m-Toluidine	58

Secondary Amines (as salts)	Dimethylamine	0
	Diethylamine	19
	Piperidine	38
	Dibutylamine	65
	Diamylamine	70
Tertiary Amines (as salts)	Trimethylamine	14
	Pyridine	42
	Quinoline	66
	Cyclohexyldiethylamine	117

Isopropyl alcohol (Isopropanol) is fairly good as a hydrogen-bonding agent. In alcohol fountain solution, isopropanol has also been used as an additive to fountain solutions to lower the surface tension (surface energy) of the fountain solution. So, using isopropanol as one of the additives of polysilicate fountain solution is attractive.

(C) Phosphoric acid.

The polysilicic acid, formed by adding acid to polysilicate, only remains stable at the pH value between 2.0 to 3.0. Although adding alcohol can retard the gelling time, adding phosphoric acid is another way to slow down the gelling. In the lithographic process, the fountain solutions usually have a pH value between 5.0 and 5.5. By adding a small amount of phosphoric acid, the polysilicic acid can remain stable with a pH value higher than 3.0.

(D) Water.

Since the F^- groups have a great effect on the precipitation of the polysilicic acid, the water used in the polysilicate fountain solution has to be water free from F^- groups. Distilled water may be used for this purpose.

Gelling Problem of the Polysilicate Fountain Solution

Polysilicic acid, formed by polysilicate, has a tendency to gelation when the pH value of the solution is below 7. Above about pH6 or 7, in the absence of soluble salts, silica bears a strong negative charge and gel formation is slow or prevented. Gelling is most rapid at pH5 to 6. From about pH2 to 5, the charge on silica or silicic acid is low, so that presumably the molecules can readily collide. Below about pH2, the rate of polymerization or gelling increases with greater acidity.[20] The polysilicate fountain solution has the same gelling problem with a pH value between 5 and 6. Therefore, by using a hydrogen-bonding agent and acid, the problem may be solved by retarding the gelling time long enough for the lithographic process with the right ratio of chemicals.

CHAPTER III

HYPOTHESIS

The hypothesis of this paper is as follows:

Using the correct ratio of lithium polysilicate, isopropanol, phosphoric acid and distilled water to formulate the fountain solution, the gelation problem of the polysilicate fountain solution can be overcome and the polysilicate fountain solution can be practical in use.

By control of the properties of silicic acid, by control of the pH value, concentration, amount of organic solvent and purity of polysilicate, one can prevent the gelation of soluble polysilicate. The optimum ratio of chemicals will make the usage of the polysilicate fountain solution practical.

CHAPTER IV

METHODOLOGY

I. Polysilicate Fountain Solution Making

(A) Using nonlinear programming functions as a pilot test guide for chemical mixing.

Assume using:

lithium polysilicate	x g
phospheric acid (86%)	y g
isopropanol	z g
water (distilled)	u g

To use as small amounts of chemicals as possible, the object is minimizing:

$$x + y + z + u$$

subject to:

(1) Because a gel can be formed containing around 200 moles of water for each mole of silica, if one does not want to form a gel, for each mole of-silica more than 200 moles of water are needed.

$$200 \times \frac{u}{18} > \frac{x}{400} \times 1$$

$\frac{u}{18}$: moles of water

$\frac{x}{400}$: moles of polysilicate

So, $\frac{200u}{18} > \frac{x}{400}$

$$\frac{100u}{9} - \frac{x}{400} > 0 \qquad (1)$$

(2) The alcohol fountain solution can be concentrated up to 30 percent. By setting the limit not less than 30%, the percentage can be lowered later by adjustment. So, the equation requires that the isopropanol concentration be less than 30%.

$$\frac{z}{x + y + z + u} > 30\%$$

$$\frac{z}{x + y + z + u} > 0.30$$

$$\frac{z}{x + y + z + u} - 0.3 > 0 \qquad (2)$$

(3) Compared to gum arabic fountain solutions, polysilicate fountain solution, using lithium polysilicate at less than 5% is reasonable. The later adjustment can be made to increase the concentration if needed.

$$\frac{x}{x + y + z + u} < 5\%$$

$$\frac{x}{x + y + z + u} < 0.05$$

$$\frac{x}{x + y + z + u} - 0.05 > 0 \qquad (3)$$

(4) Because lithium polysilicate is a material with pH values close to 7, the pH value depends on the phospheric acid (H_3PO_4).

$$\begin{array}{ccc} H_3PO_4 \longrightarrow & 3H^+ & + \ PO_4^{\equiv} \\ A - a & 3a & a \end{array}$$

A : H_3PO_4 before dessociation (molar)

a : dissociated H_3PO_4 (molar)

$$Ka = \frac{[H^+]^3 [PO_4^{\equiv}]}{[H_3PO_4]}$$

$$Ka = Ka_1 \times Ka_2 \times Ka_3$$

$$\text{Since } Ka_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.52 \times 10^{-3}$$

$$Ka_2 = \frac{[H^+][HPO_4^{=}]}{[H_2PO_4^-]} = 6.22 \times 10^{-8}$$

$$Ka_3 = \frac{[H^+][PO_4^{\equiv}]}{[HPO_4^{=}]} = 1.72 \times 10^{-12}$$

So, $Ka = 7.52 \times 10^{-3} \times 6.22 \times 10^{-8} \times 1.72 \times 10^{-12} = 7.952 \times 10^{-22}$

$$Ka = \frac{a^3 \cdot a}{A - a}$$

$$A = \frac{0.86 \times \frac{y}{98}}{\frac{x + y + z + u}{1000}}$$

$\frac{y}{98}$: moles of phospheric acid

$\frac{x + y + z + u}{1000}$: approximate liters of lithium polysilicate solution.

$$Ka = \frac{a^3 \cdot a}{\frac{0.86 \times \frac{y}{98}}{\frac{x + y + z + u}{1000}} - a}$$

$$7.952 \times 10^{-22} = \frac{a^4}{\frac{0.86 \times \frac{y}{98}}{\frac{x + y + z + u}{1000}} - a}$$

because a is a very small number, the equation can be rewritten as:

$$7.952 \times 10^{-22} = \frac{a^4}{\dfrac{0.86 \times \dfrac{y}{98}}{\dfrac{x + y + z + u}{1000}}}$$

$$a^4 = 6.978 \times 10^{-21} \times \frac{y}{x + y + z + u}$$

$$a = (6.978 \times 10^{-21} \times \frac{y}{x + y + z + u})^{1/4}$$

The pH value needs to be higher than 3.5, otherwise the fountain solution is not practical for lithographic use. So, setting pH values between 3.5 and 4.0 first, it can be made higher by reducing the amount of phospheric acid at the final adjustment.

$$10^{-4.0} < 3a < 10^{-3.5}$$

$$3(6.978 \times 10^{-21} \times \frac{y}{x + y + z + u})^{1/4} - 10^{-3.5} > 0 \qquad (4)$$

$$3(6.978 \times 10^{-21} \times \frac{y}{x + y + z + u})^{1/4} - 10^{-4.0} < 0 \qquad (5)$$

(B) A nonlinear programming package is used to solve the problem.

By using OPTIVAR*, the computer output to minimize subject to equations (1), (2), (3), (4), (5), is as follows:

	x	y	z	u
	0.1	0.0308	3.607	8.235
the ratio	0.835%	0.257%	30.127%	68.781%

*OPTIVAR is a name of nonlinear programming package. Please see more detail in Appendix A.

The pilot test was done by controlling the ratio according to the computer output: mixed 2.5 g lithium polysilicate with 180 g distilled water, 1 g phospheric acid and 70 g isopropanol. The pilot test showed a good solution without gelling for more than a day with the pH value of 4.0 which is encouraging.

Because some other variables may affect the property of polysilicate fountain solutions, one may obtain a more stable solution without gelling with some small adjustments. The computer output is simply a direction for further experiments.

(C) Making the small change to get better ratio.

The small adjustment should produce a higher pH value with a lesser amount of isoprapanol and a little more lithium polysilicate. All of the above is to obtain a better working fountain solution for lithography and to make the polysilicate fountain solution closer to the alcohol fountain solutions which have been used. After a series of tests in the lab, polysilicate fountain solution could be reduced so that the amount of isopropanol was 10% and the amount of lithium polysilicate increased to 3% and only 0.05% of phosphoric acid (86%) was used with 86.95% of distilled water. The experiment showed it would not gel for more than a week.

Press Testing

Testing was done with the f.s. formulation obtained by the computer (page 22) and with f.s. formulation varied as shown on page 23 for the purpose of testing the criticality of f.s. formulation.

The press testing requires data as to the non-image area and image area on the plate. The non-image area test had been done by counting how many plate revolutions the plate needed to pick up a solid scum. The polysilicate fountain solution versus the regular alcohol fountain solution (5% of isopropanol) on the non-image area were compared. The non-image area picked up the fountain solution and let the scum be picked up by the ink form rollers. The difference in the number of revolutions to clean the plate with each of the two kinds of fountain solutions determine which kind is better.

The image area was evaluated with the polysilicate fountain solution on the dampening tray by collecting the first acceptable sheet and the sheet after running for more than 1500 impressions. Comparing the image area (especially the solid part of the images) the printer checked to see if there were any blind areas appearing in the image area. It indicates whether the polysilicate fountain solution gels or does not gel on the running press.

The press test work was done on a ATF Chief 15 Duplicator with a new 3M dampening sleeve. The plates used were Enco N-25 negative working plates. The image was a tint guide from Bata Screen Corp. The ink was GPI Sunlite Coated Black made by Sun Chemical Corporation's General Printing Ink Division. The paper was long grain 8½"x11" white bond with 20 substance made by Data Com Inc. for Xerox copy use. The regular alcohol fountain solution used was a mixture of 2 oz. of RBP Blue Polyonic Fountain Solution with water and 5% of isopropanol (about 150 c.c.) to make a gallon of working fountain solution. The pH value of this fountain solution was around 3.8.

The polysilicate alcohol fountain solution used was 3% of lithium polysilicate with 10% of isopropanol, 0.1% of phosphoric acid and 86.9% of distilled water. The pH value of this fountain solution was around 3.4.

The press was set carefully to give a satisfactory impression. All the settings on the press were changed at a minimum before the completion of a series of tests. The machine speed was constantly set at 3000 rph. The ink volume control of the inking system had been set one notch above "stop." The moisture volume control of the dampening system was set at the minimum level.

(B) Procedure.

The non-image area press test.

(1) Placed the fountain solution inside the dampening tray.

(2) The gummed up plate was sponged free from excess gum with the fountain solution.

(3) Lifted up the dampening form roller.

(4) Turned the machine power switch to "ON" position.

(5) Ran the Chief 15 for several revolutions until the ink and fountain solution spread evenly on the rollers.

(6) Made sure the plate was clean and dry.

(7) Inked the plate with full solid ink by 10 revolutions of the plate by moving the moisture-ink control lever to "ink" position.

(8) Lowered the dampening form roller to the plate.

(9) Counted how many revolutions were needed for the plate to become clean in non-image areas.

(10) Moved the moisture-ink control lever to "OFF" position and turned the machine power to "OFF" position.

(11) Washed the plate with Enco plate cleaner and water.

(12) Gummed up the plate with Enco GS gum solution.

(13) Cleaned the blanket and fountain rollers.

(14) Started from step (1) again if the fountain solution was changed. Otherwise, started from step (2) again until the completion of the tests.

Image area press test.

(1) Placed the polysilicate fountain solution inside the dampening tray.

(2) The gummed up plate was sponged free from excess gum with the polysilicate fountain solution.

(3) Turned the machine power switch to "ON" position.

(4) Ran the Chief 15 for several revolutions until the ink and polysilicate fountain solution spread evenly on the rollers.

(5) Made sure the plate was clean and did not have an excess of fountain solution.

(6) Moved the moisture-ink control lever to "moisture" position. Allowed the plate cylinder to revolve one or two revolutions.

(7) Moved the moisture-ink control lever to "ink" position. Allowed the plate cylinder to revolve several revolutions until the image area picked up ink and offset to the blanket.

(8) Turned the vacuum feeder power switch to "ON" position and allowed the paper to pass.

(9) Picked up and collected the first acceptable sheet.

(10) Let the machine run for more than 1500 impressions.

(11) Picked up and collected another acceptable sheet.

(12) Turned the vacuum feeder power switch to "OFF" position and them moved the moisture-ink control

lever to "OFF" position and turned the machine power off.

(13) Washed the plate and then gummed the plate.

(14) Cleaned the blanket and fountain rollers.

(15) Replaced the fountain solution, ready for next test.

Data Collection and Discussion

The press test for the polysilicate fountain solution after the small change in the fountain solution formulation showed blinding of the image area. Although the ink scum picking test was very good, the printout material showed poor quality in the solid area and in the halftone area.

Assuming that failure might be caused by using too much lithium polysilicate, a series of tests were done to find the best ratio. With isopropanol lowered to 5%, lithium polysilicate lowered to 0.8%, and phosphoric acid (86%) lowered to 0.01%, the polysilicate fountain solution could be used without any blinding of the image area. The following data for the non-image area press test was based on the ratio above. Both used plate revolutions as their units, (Table II).

TABLE II

Data Comparison for Polysilicate Fountain Solution and Regular Alcohol Fountain Solution in Number Revolutions Needed to Clean Out Non-Image Area of Plates

Test Number	Polysilicate Fountain Solution (pH = 3.7)	Regular Alcohol Fountain Solution (pH = 3.8)
1	18	18
2	20	17
3	22	20
4	24	21
5	20	15
6	16	23
7	18	20
8	20	23
9	20	18
10	16	21
11	14	16
12	22	20
13	18	19
14	16	20
15	20	21
16	22	22
17	18	16
18	18	18
19	19	15
20	21	22

$\bar{X} = 19.1$ $\bar{X} = 19.25$

$n = 20$ $S_d = 3.11659$ $\bar{d} = 0.15$

By using tests of paired data with standard deviation unknown, the "student's t distribution" value in this case equals 0.21524.* Since this value does not exceed the critical value at the 0.05 level of the two-tail critical value (2.0930), one can say these two kinds of fountain solution have no significant difference.

The statistical analysis can affirm the reliability of the test results up to 95%. It indicates that the polysilicate fountain solution can be practical in use.

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*according to the equation $$t_v = \frac{\bar{d}}{s_d/\sqrt{n}}$$ 21

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

I. Summary and Conclusions

This thesis set out to discover whether a fountain solution containing a polysilicate can be used as a replacement for the traditional gum arabic solution. Acidic silicate solutions will gel in the fountain, and this problem was seen as the major area of concern of this paper.

The hypothesis states that by using the correct ratio of lithium polysilicate, isopropanol, phosphoric acid and distilled water in the formulation of the fountain solution, the gelation problem can be overcome, and that practical use can be made of such a solution as a result.

By controlling the properties of silicic acid such as pH value, concentration, the amount of organic solvent and the purity of the polysilicate, it is possible to prevent the gelation of soluble polysilicate. The optimum ratio of chemicals can make practical the use of such formulations as fountain solutions.

The formulation used for the press test was 0.8 percent lithium polysilicate, 0.01 percent phosphoric acid, 5.0 percent isopropanol and 94.18 percent distilled water. Using this formulation, the gelation problem can be minimized so that the solution can be used as a practical replacement for gum fountain solutions. The problem of blinding of image areas can also be avoided by using the proper amount of lithium polysilicate in the solution.

The results obtained from experimentation show that the hypothesis is supported, and that it is therefore possible to formulate a functional polysilicate fountain solution.

II. Recommendations for Future Investigation

Because of good hydrophilic property, one may find an optimum ratio for the lithium polysilicate fountain solution with different kinds of printing machines. According to the press test done for this paper, the ratio is critical for good running conditions. The latitude of the ratio change is small and narrow. Too much lithium polysilicate in the polysilicate fountain solution can cause blinding of the image area and can lower the ink transfer from the blanket to the paper. But if a good ratio has been found, the ink and water balance will be much easier to control by the press operator.

Another critical thing, according to the press tests done is the pH value. The lithium polysilicate fountain solution can cause the plate to carry too much water if the pH value is lower than 3.3.

Different kinds of acids, polysilicates and hydrogen-bonding agents may be introduced to the polysilicate fountain solutions to make a better working polysilicate fountain solution. All of the above suggest further investigations of the polysilicate fountain solution.

FOOTNOTES

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OPTIVAR

DESIGNERS' OPTIMIZATION SUBROUTINES

USER'S MANUAL

by

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1. INTRODUCTION

The objective of this package is to make optimization as simple as possible for practicing designers. Almost all of the subroutines are called in a very similar way; the calling program in its simplest form is very short and fully prescribed; the various subroutines are independent and easily adapted to a design package for a particular device; and the coding is machine independent and should be easily adapted to any computer. The designer need not, in fact, know more than a minimum of computer programming or optimization theory. However, it is desirable to develop some familiarity with both, particularly for larger and more complicated problems.

The chapters are grouped in related sets as shown in the chart below.

GENERAL INFORMATION ON HOW TO USE THE PROGRAMS	2. Description of Nonlinear Programming System of Subroutines and How to Use
	3. Service Subroutines - UREAL, EQUAL, CONST
	4. Fortran Subroutines for Penalty Functions for Constrained Minimization
Unconstrained Nonlinear Methods All Using the Same Interchangeable Penalty Functions	5. ADRANS
	6. DAVID
	7. FLETCH

	8. JO
	9. PDS
	10. SEEK
	11. SIMPLX
Constrained Nonlinear Methods	12. APPROX
	13. RANDOM
	14. REDUCE
Single Variable Minimization	15. FMIN
Linear Programming	16. SIMPLE
Random Number Generator	17. FRANDN

For more information on the practice and mathematics of optimization the reader is referred to the following selections from the extensive literature.

Avriel, M.: *Nonlinear Programming; Analysis and Methods*, Prentice-Hall, 1976.

Gill, P.E. and W. Murray (editors): *Numerical Methods for Constrained Optimization*, Academic, 1974.

Murray, W. (ed.): *Numerical Methods for Unconstrained Optimization*, Academic, 1972.

Stark, R.M. and R.L. Nichols: *Mathematical Foundations for Design; Civil Engineering Systems*, McGraw-Hill, 1972.

Greenberg, H.J. (ed.): *Design and Implementation of Optimization Software*, Sijthoff & Noordhoff, 1978.

2. DESCRIPTION OF NONLINEAR PROGRAMMING SYSTEM OF SUBROUTINES AND HOW TO USE

General Philosophy

The philosophy underlying the nonlinear programs is that no one strategy can be relied upon to be best for any given problem. Although some methods more commonly do better than others, it is not possible to predict in advance which is the best one to use. There is always some unknown best match between problem and optimization strategy. It is therefore desirable to structure the programs so that they are very easy to call by a simple calling program, and each one is called in a very similar way, so that the user can rapidly switch from one to another.

The structure of the programs is also based on the hypothesis that there is an optimal match among the problem, the unconstrained optimization strategy, and the strategy for handling constraints. To this end it is possible for most unconstrained methods to call any one of four or five penalty functions, and the reduced gradient method can use alternate methods to establish search directions.

Experienced optimizers will likely tend to settle on a few favorite combinations, but the user is cautioned against relaxing his or her vigilence in searching out the ideal combination for a problem in an unfamiliar area.

A further argument for trying several methods is the improved credibility of the solution if more than one converges to the same solution.

The structure of the program has other important advantages.

1. Combinations of strategies can be used in one run by means of a simple user written calling program.
2. Data for trade-off curves can be generated by means of a simple DO-loop in the calling program.
3. They are easily integrated with user oriented design packages.
4. Input data can be easily generated in the calling program.
5. In its simplest form, the calling program is easily prescribed and requires little knowledge of programming from the user.
6. The user can use standard output, or his or her own output, as desired.

It is important to note that no input parameters are redefined after a computer run of any optimizing subroutine, except the array XSTRT, which contains the starting value for the search strategy. All methods (except RANDOM which does not use a starting value) return the final optimum value in XSTRT (as well as in X). This is convenient in runs combining different methods, and in runs for developing trade-off curves. If a method fails, XSTRT is not redefined.

How to Use the Subroutines

In its simplest form the user must provide a simple calling program defining the input data, calling the desired optimization strategy, and calling ANSWER, the standard output subroutine. The optimization and constraint functions are defined by the user written subroutines UREAL, CONST and EQUAL.

The procedure is described in detail below and illustrated by a simple example.

1. Write the calling program. In its simplest form it is as follows.

(a) DIMENSION statement - check through the list of input, output and working variables. Include all subscripted variables, dimensioning as indicated.

(b) Define input data. Include DATA cards, or READ statements, or individual cards such as

```
N = 4
```

so that each variable in the input list is defined, unless default options are used. If any one of the default options is not used then the COMMON statement for the subroutine must be included.

(c) Call the subroutine. For example

```
CALL RANDOM(N,NCONS,RMAX,RMIN,X,U,PHI,NVIOL,W)
```

(d) Call ANSWER to give printed output.

(e) Add STOP and END.

2. Write subroutine UREAL to define optimization function.

3. Write subroutines CONST and EQUAL to define constraints.

If there are no constraints of one type or the other, the compiler may still require a dummy program.

4. Add to the deck all subroutines called, as listed at the end of the documentation for each method subroutine.

Example:

Required to minimize the objective function

$$U = X_1^2 + X_2^2 - 6.0\ (X_1 + X_2) + X_3$$

Subject to the constraints

$$X_1 \leq 10.0$$

$$X_3 \geq 1.0$$

The following program MAIN with subroutines UREAL and CONST demonstrate a suitable program for the solution of this problem. The method selected for optimization has been the direct search strategy of SUBROUTINE SEEK. In this example all default options are used for the programming parameters F, G, MAXM, NSHOT, NTEST, IPRINT, IDATA. If the user wished to specify IPRINT = 0, for example, the following additional statements would be required.

```
     COMMON/SEEK/IDATA,IPRINT,NSHOT,NTEST,MAXM,F,G,TOL,ZERO,
     R,REDUCE
     IPRINT = 0
```

The other parameters (TOL, ZERO, R, REDUCE) arise from the penalty functions used.

```
 DIMENSION X(3),XSTRT(3),RMAX(3),RMIN(3),PHI(2),PSI(1),W(24)
 N=3
 NCONS=2
 NEQUS=0
 NPENAL=5
 DATA RMAX/10.,10.,10./
 DATA RMIN/0.,0.,0./
 DATA XSTRT/5..5..5./
 CALL SEEK(N,NCONS,NEQUS,NPENAL,RMAX.RMIN,XSTRT,X.U,PHI,PSI,NVIOL.W
1)
 CALL ANSWER(U,X,PHI,PSI,N,NCONS,NEQUS)
 STOP
 END

 SUBROUTINE UREAL(X,U)
 DIMENSION X(1)
 U=X(1)*X(1)+X(2)*X(2)-6.*(X(1)+X(2))+X(3)
 RETURN
 END

 SUBROUTINE CONST(X,NCONS,PHI)
 DIMENSION X(1).PHI(1)
 PHI(1)=10.-X(1)
 PHI(2)=X(3)-1.
 RETURN
 END
```

Executing this program on a CDC 6400 computer gave the solution:

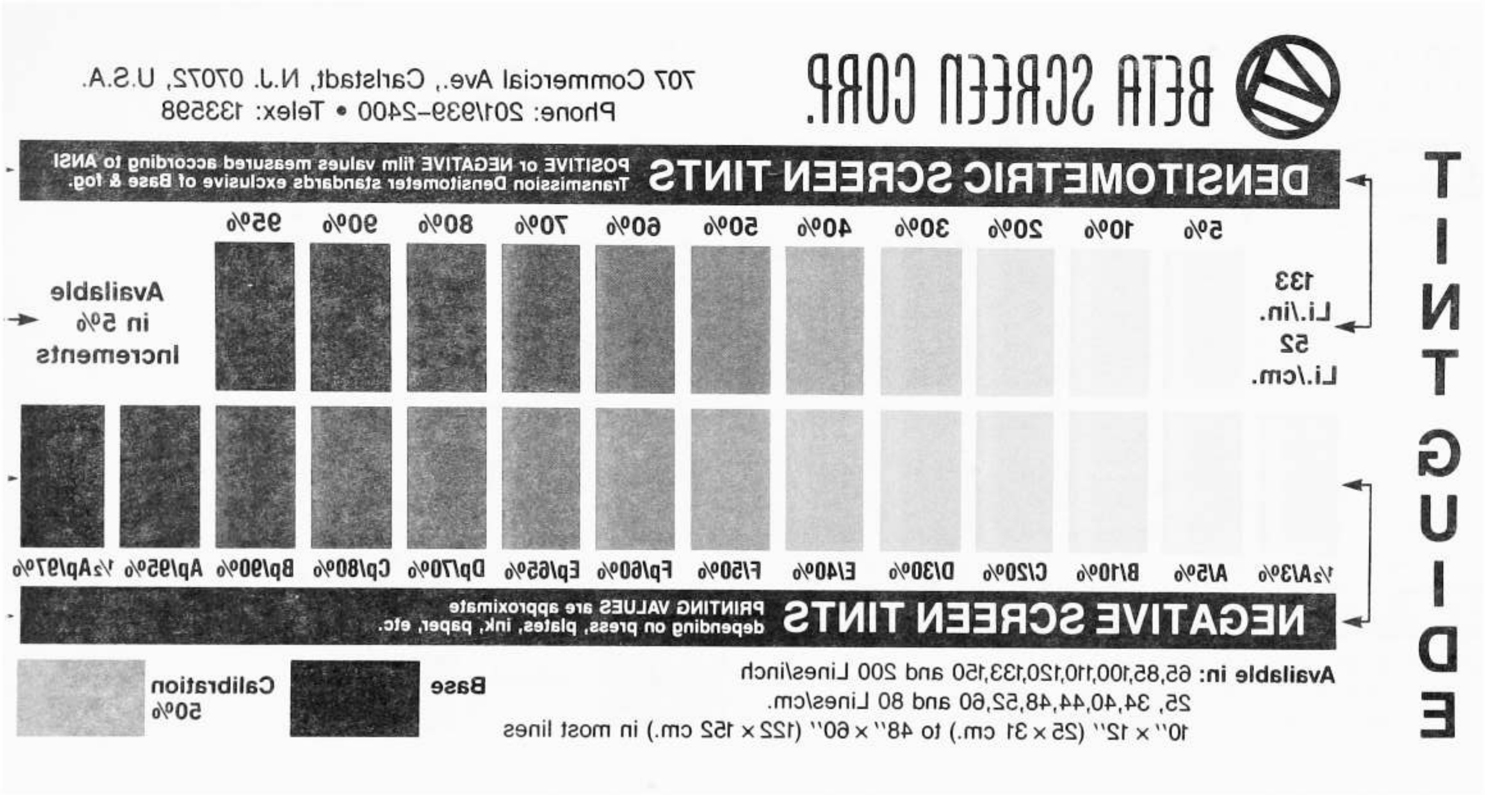
```
                              OPTIMUM SOLUTION FOUND
                           MINIMUM  U =  -.17000000E+02

                                 X( 1) =   .30000000E+01
                                 X( 2) =   .30000000E+01
                                 X( 3) =   .10000000E+01

INEQUALITY CONSTRAINTS
                               PHI( 1) =   .70000000E+01
                               PHI( 2) =  -.87396755E-12
```

The user written programs can, of course, be much more complex than this, incorporating features described above. However, the basic requirements are as prescribed by the example with respect to subroutine arguments, DIMENSION statements, and data input.

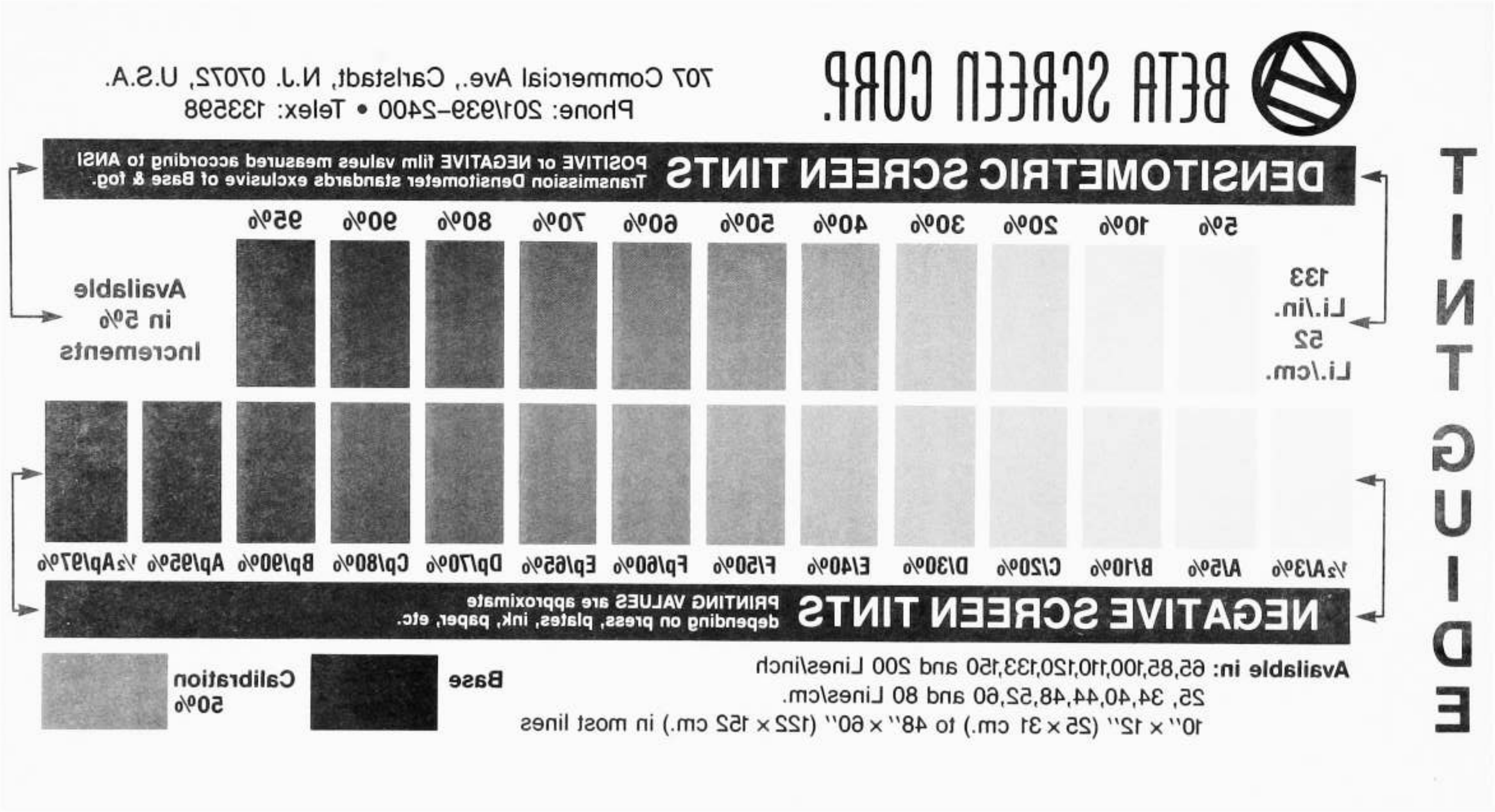
Subroutines UREAL, EQUAL, CONST and ANSWER are more formally described in Section 3.

IT IS VERY IMPORTANT FOR THE USER TO AVOID USING ANY FORTRAN VARIABLES THAT ARE IDENTICAL TO ANY OPTIVAR SYSTEM VARIABLES.

Alcohol fountain solution at 3000 RPH
(pH = 3.8)



Polysilicate fountain solution at 3000 RPH (PH=3.7)



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10'' × 12'' (25 × 31 cm.) to 48'' × 60'' (122 × 152 cm.) in most lines

polysilicate fountain solution at 7000 RPH
(PH = 3.7)