A DURABLE WATERLESS PLANOGRAPHIC PLATE

Fred Dankert*

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Abstract: A Waterless planographic plate is described which is more durable than commercial planographic plates to this date. The durability is obtained by causing a silicone polymer to form a chemical bond to aluminum oxide as found on litho plates. The method for producing a precise Dimethylsiloxane polymer stencil depends on producing a solvent permeable coating over a developed litho plate. A suitable solvent is used to penetrate the coating thereby dissolving the image and releasing the silicone polymer from exactly those locations. After washing and lacquering the plate is post cured at elevated temperature. The finished plate was tested for contact angles, coefficient of friction, and rub/abrasion tests. It was also printed with Waterless type offset inks. It is possible to produce such plates photographically or by direct digital imaging.

Introduction

Waterless Planography depends on altering the surface of a plate so that the image has high free surface energy and the nonprint areas have low free surface energy. Dimethylsiloxane polymers have the appropriate low free surface energy. Various methods have been used to obtain proper placement of these polymers in the non print areas, usually by photographic means. In most

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• IMCON Research Printing, RR #3, Box 99, Oxford, NY 13830, (607) 843-5130 (FAX 607 843-2130)

cases the photographic imaging material is between the metal substrate and the silicone polymer. Since dimethyl siloxanes do not bond well to organic surfaces special techniques have to be employed to obtain sufficient adhesion. None of these methods are totally satisfactory so that plates made this way are subject to mechanical wear and failure. This paper describes a way to circumvent this problem by bonding the silicone polymer directly to the metal oxide substrate.

The **schema** is as follows:

1. A litho plate is exposed and developed, but not gummed.

2. A silicone coating is applied to the plate and heat cured.

3. A solvent/developer is applied to the plate. This penetrates the cured silicone and dissolves the image. Thus the silicone is released from the image.

4. The plate is washed with water and dried.

5. A lacquer is applied to the image.

6. The plate is post cured.

7. After cooling the plate is ready to print.

To understand how the method works it is useful to consider **silicone** and **metal oxide chemistry.**

Aluminum and stainless steel (as well as other metals and plastics not discussed here) are suitable substrates if their surfaces are properly treated before hand. What we seek is a metal oxide partially hydrated surface. Anodized aluminum has such a surface; especially so if it has been sealed. The sealing may be accomplished in a number of ways, including silicating as commonly practiced in litho plate manufacture. Anodizing may be carried out in various electrolytes. Sulfuric and phosphoric acid electrolytes produce satisfactory surfaces. It is also possible to produce the proper surface by chemical treatment. In each case Aluminum oxide partially hydrolyzed is the preponderant species. Aluminum oxide and the fully hydrolyzed oxide are present in lesser amounts. Other compounds such as sulfates and phosphates are present in smaller quantities.

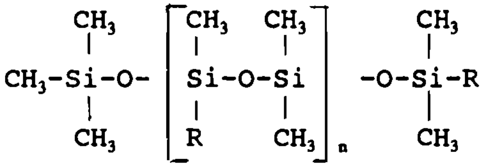
(1)

Al_2O_3 = Aluminum oxide
$AlO(OH)$ = Aluminum oxide partially hydrolyzed
$Al(OH)_3$ = Aluminum oxide fully hydrolyzed

Stainless surfaces are principally Chromium oxide and hydrated Chromium oxide. The chemistry is very similar to that of anodized aluminum.

Di methyl siloxane polymers may have reactive terminal and pendant groups as follows:

(2)

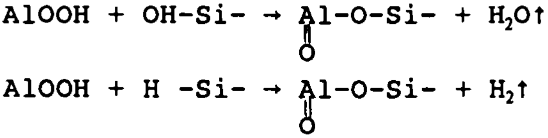


$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{R}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\right]_n-O-\underset{CH_3}{\overset{CH_3}{Si}}-R$$

Where R=H, OH, CH_3O, $CH_2=CH_2$

Those **polymers** with H or OH groups will react directly with Aluminum oxide hydrate.

(3)



$$AlOOH + OH-Si- \rightarrow \underset{O}{\underset{\|}{Al}}-O-Si- + H_2O\uparrow$$

$$AlOOH + H-Si- \rightarrow \underset{O}{\underset{\|}{Al}}-O-Si- + H_2\uparrow$$

In practice water and hydrogen are not actually given off, but react with other aluminum, oxide species and other sites on the silicone polymer.

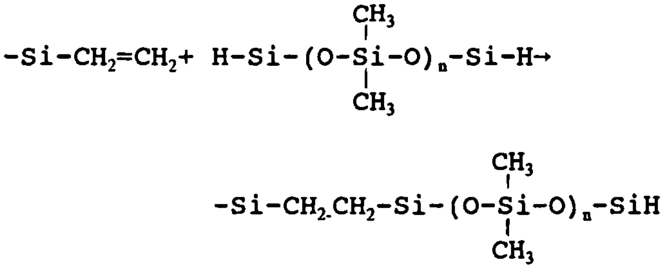
When the polymer contains methoxy groups the reaction must have water present to hydrolyze the methoxy groups to hydroxyls, which in turn react with the aluminum oxide hydrate.

(4)

$$Si{-}OCH_3 + H_2O \rightarrow {-}SiOH + CH_3OH\uparrow$$

When the polymer contains vinyl groups there must be present a crosslinking compound which links the polymer to a silicone capable of reacting with the aluminum oxide species.

(5)



$$-Si-CH_2{=}CH_2 + H-Si-(O-\underset{CH_3}{\overset{CH_3}{Si}}-O)_n-Si-H \rightarrow$$

$$-Si-CH_2CH_2-Si-(O-\underset{CH_3}{\overset{CH_3}{Si}}-O)_n-SiH$$

In the **first step** an anodized aluminum plate that has been sealed is coated with a light sensitive coating. This may be a litho plate as supplied to the trade or aluminum specially treated and coated with light sensitive coatings. Since most litho plates are mechanically grained they loose some capacity for high resolution. The graining also reduces contact angles of inks. Smoother plates are more disireable. Two alloys of aluminum were tried (1000, 3003). After chemical treatment or anodizing and sealing no substantial difference was noted.

Light sensitive coatings were coated on the prepared aluminum plate. Roller coating and plate whirling techniques were employed to produce a smooth coating. The thickness was not crucial; the amount normally found on presensitized litho plates is adequate. Negative and positive working coatings were used. The coating must be made with resins which after litho development remain soluble in the solvent used to develop the silicone stencil. After the **plate is exposed** with UV light and developed in the prescribed manner for litho plates, it is washed with water and dried. No gumming is employed. The **silicon coating is applied** in the manner that is used when gumming litho plates. The coated plate is heated to 300°F and held for 2 minutes. After cooling a second coating of the silicone is applied and cured the same way. The first coating acts as a primer for the second. It is believed the second coating aligns itself with siloxane chains facing up thereby reducing free surface energy.

Once cooled the plate is developed by pouring developing **solvent on the plate.** This solvent is chosen from solvents of medium polarity with a solvent parameter of about 12. N-Methyl pyrollidone is suitable. The developing solvent penetrates the cured silicone where there is image underneath. The image material dissolves in the developing solvent and is lifted from the aluminum substrate. Such silicone coating as was above the image is also released. A water wash takes away all dissolved image and released silicone, leaving a very **precise silicone polymer stencil** adhering to the hydrated aluminum oxide. At this point a **protective lacquer** is applied. When dry the plate is washed with a low KB aliphatic solvent, which removes the lacquer from the silicone non-printing areas. Without the lacquer the bare aluminum oxide surface when baked at high temperature tends to become oleophobic and resists ink. Post **curing** at 400°F fully for 5 minutes hardens the silicone coating.

The silicone coating is composed of a combination of **Dimethyl siloxane oligomers** with **reactive terminal** and **pendant groups. Tin catalysts** accelerate the cure. Post curing is facilitated by excess silicone hydride groups on the oligomers. It is important that the initial cure produces a permeable polymer, which permits development by allowing the developing solvent to penetrate to the original image material.

Contact angle measurements were made on the cured silicone coating. Using the procedure outlined in the 1991 TAGA paper of Krishnan and Klein the free surface energy falls in the range of 10 to 12 dynes/con.

Friction tests were made. The coefficients of friction were 0.39 + 0.38 for static and kinetic friction. A comparable commercial Waterless plate had readings of 0.77 + 0.68. I attribute this difference in coefficient of friction to differences in film thickness and internal bonding. To obtain film integrity silicone plates made with the photo sensitive coating between the silicone and the plate must be relatively thick. Thick silicone polymer films tend to have a rubbery, elastic nature. Silicone bonded directly to aluminum oxide are much harder; showing very little elastic modulus.

Rub resistance tests were carried out on a 10-lb. rub test. The silicone plates described in this paper which are bonded to aluminum oxide are considerably more rub resistant than commercial silicone plates. This rub resistance combined with low coefficient of friction will produce a more durable plate.

The aluminum oxide bonded plates are also much more **solvent resistance.** Hydrocarbon solvents such as commonly used to wash presses and blankets have been used to wash out these plates twenty times without failure of the surface. Even strong solvents such as toluene have been used without causing failure.

Resolution tests were conducted by making Waterless plates from positive litho plates. Cookson Graphics Capricorn plates were exposed to film made of GATF of Agfa Select Set 5000 from 2400 Cristal Raster.

Inks were made according to the author's formulas. These inks have heat tolerance equal or superior to Dainippon highest heat Waterless inks.

Prints were made on a Consolidated 140 Offset Proof Press. Examination under magnification shows resolution of plates to be similiar to the original GATF photo proofs. The prints show resolution typical of offset transfer of Waterless inks.

Another advantage of this process is the ability to produce plates from images other than those photographically derived. It is possible to **hand draw images** directly on the plate before the silicone coating has been applied. Images at that stage are equally easy to remove with solvent. Utilizing these principals plates were made using **xerographic toner** as the imaging material. The plates are then directly converted to a silicone Waterless plate by the same means described earlier in this paper. It is therefore possible to produce plates directly from digital data, thereby **circumventing photography** altogether.

Conclusion

It is possible to produce a rub resistant **Waterless** planographic plate by reacting a **silicone polymer** with the **aluminum oxide** surface of aluminum litho plates. The procedure outlined produces a **high resolution silicone polymer stencil chemically bound** to the plate. This low free surface energy plate has a low coefficient of friction, and is solvent resistant.

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The Graphic Arts Technical Foundation supplied sets of Agfa Select Set 500 and 2400 Cristal Raster color separations which were used in the resolution tests.

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