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FABRICATION OF FAST TURN-AROUND INDIRECT-DIRECT THICK FILM SCREENS

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ABSTRACT

The preparation of Indirect-Direct thick film screens can be streamlined using principles known for quite some time but often overlooked. A method of obtaining long durability screens at low cost is described after a suitable review of dichromated colloids. Control of the thickness of the sensitized layer is explained as well as long range storage enabling a quick and efficient turn-over in the fabrication of thick film screens.

INTRODUCTION

Several methods are currently used for the preparation of thick-film screen viz the direct, the indirect, the indirect-direct methods and metallic stencils.

Direct Method

A layer is built-up on the screen mesh entirely from light sensitized colloids which are dried, exposed and developed while mounted on the screen mesh. Dichromated and diazo materials are used. The patterned screen offers excellent durability and resolution; however, considerable skill is required to deposit consistent layers. Thickness difficult to control but is low.

Indirect Method

An emulsion supported on a thin plastic film is patterned before being affixed to the screen mesh, then applied to the screen while still wet. Diazo materials are commonly used. The method is convenient, quick and has reasonable resolution, but low durability. Low cost.

Indirect-direct Method

A layer is built up on the screen mesh using an emulsion originally supported by a thin plastic backing film. The layer is patterned while mounted on the screen using either dichromated or diazo light sensitizers. The method has the advantage of the easy thickness control of the indirect method, while retaining the durability and resolution of the direct method. Low cost.

Metallic Stencils

The stencils can be formed with metallic sheets instead of organic emulsions. A large variety of methods exist but all are complex and slow compared with the preceeding methods; however the durability is largely improved and the resolution is excellent. These screens are somewhat sensitive to mishandling.

Only the indirect-direct method will be dealt with here since it offers a good compromise among all the methods available. The chosen sensitizer is of the dichromate variety, which has been known for the past 135 years and used with considerable success in a multitude of photomechanical reproduction methods.

DICHROMATED COLLOIDS (1-5)

In 1839 Mungo Ponton (1801-1880) discovered in Scotland the sensitivity to light of paper impregnated with potassium dichromate. Some years later in 1845 Edmond Becquerel (1820-1891) a French physicist, experimented with dichromated starch, gelatin, casein and albumine and established their insolubility in water after exposure to light. In 1852 Fox Talbot (1800-1877) independently discovered in England the light sensitivity of dichromated gelatin and patented photoglyph an heliographic printing process (photogravure) using etching on steel or copper. From there on dichromated colloids were established as photoresists, photographic emulsions including colour slides and stencils, and are still used as such today. New applications and improvements

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are still found (7 and 14) and old processes are from time to time brought back to new life such as the carbon process which some claim produces the best photographic prints since 1864.

Silk-screen was used during the 19th century in Europe for the production of printed materials. Silk-screen printing has been used for many centuries in Japan and China. Nevertheless the first photographic production of silk-screen stencils is somewhat recent and is attributed to the R.A.F. during the first world war to disseminate reconnaissance sketches. The formation of an image on silk-screen with dichromated gelatin is surprisingly recent since it waited until the second world war (8). Many organic colloids, natural and synthetic, have been used in photomechanical printing during the past century as shown in Table 1.

DICHROMATES

All chromates or dichromates which are soluble in water can form photosensitive layers in combination with organic colloids. In practice only a few dichromates are used.

Ammonium dichromate $(NH_4)_2\ Cr_2O_7$

This is the most commonly used dichromate since it is the most sensitive to light. Aqueous solutions of ammonium dichromate are soluble in some common organic solvents and these solutions are often sensitive to light unlike the aqueous solution alone which is not. Ammonium dichromate is flammable and can explode in contact with many substances. Around 120°C can explode to form green chromium dioxide, water vapour and nitrogen.

Potassium dichromate $K_2\ Cr_2O_7$

This dichromate is also soluble in water but not in common organic solvents. The sensitized colloids are often slightly less sensitive to light than when sensitized with ammonium dichromate.

Sodium dichromate $Na_2\ Cr_2\ O_7.\ 2H_2O$

This dichromate is seldom used. Slow.

A word of caution in handling dichromates is in order since these are toxic and may cause ulcers from prolonged contact on the skin, or contact with open wounds. The dichromates are absorbed through the skin and act as protein precipitant which ultimately results in local ulcers. A wash in a dilute solution of bisulfite or dilute hydrogen peroxide is recommended to neutralize the absorbed dichromates in the skin, particularly if the skin is cut. After repeated contamination a rash develops followed by ulceration if hygiene is neglected.

Photochemical Hardening of Dichromated Films

The mechanism of reaction is yet to be explained satisfactorily after a century of practical use. Several theories have been advanced on decomposition of dichromates in presence of oxidable organic matter into neutral chromates and chromic chromates which are further decomposed into chromic acid and chromium oxide by washing, Figure 1. The practical aspect remains that dichromated organic colloids normally soluble in water becomes insoluble after exposure to light. Light appears to accelerate an insolubilization which occurs slowly in the dark (dark reaction).

The spectral sensitivity is influenced little by the nature of the colloid; however differences appear from the spectral absorption of the colloid. The sensitivity to light is almost proportional to concentration of the dichromate with an upper limit brought by crystallization at the surface of the colloid, Figures 2 and 3. The light absorption varies with the pH i.e., decreases as the pH increases hence the pH must be controlled (often done by addition of a chromate or ammonia which converts the dichromate into neutral chromate).

The insolubilization starts at the outer surface and progresses deeper into the coating as exposure increases, this is to be expected from the Grotthus-Drafer law which states that only radiations which are absorbed can result in a photochemical reaction hence the upper part of the layer shields the lower part, Figure 4. Thicker layers require longer exposure to penetrate to the screen level. The maximum thickness is limited by absorption of the upper part of the layer acting as an optical filter. This phenomena is easily verified by exposure and development of a gray scale which is reproduced by control of the emulsion thickness after development.

Dark Reaction

Ammonium dichromate aqueous solutions and organic colloids are stable when kept separately. When mixed, reaction starts immediately, this reaction is called dark reaction to distinguish it from the light induced reaction, Figure 5. The dark reaction is slow and dependent on pH and temperature. The sensitized layer on the screen ages, i.e., becomes more and more insoluble in water, hence becomes useless after a few days. The dark reaction net effect is somewhat comparable to a pre-exposure. A high pH reduces the speed of the dark reaction therefore must be controlled, however it must be noted that control of the pH by addition of ammonia, commonly used with gelatin, is detrimental to the polyvinyl alcohol colloid.

Influence of Temperature on Dark Reaction

A dependence of the rate of the dark reaction with temperature had been noted as early as 1905 (9). The effect is to be expected since temperature usually increases rate of chemical reactions in some exponential manner, usually an increase of 10°C doubles the rate of reaction. This rate increase was indeed confirmed for dichromated colloids on aluminum (10) and deep-etch zinc plates (11). It was also shown by the Lithographic Technical Foundation workers that dichromated albumin and Gum Arabic reactions are almost stopped when stored at 3°C and 72% relative humidity at a cost of a small drop in gamma (relations between the illuminance and the optical density). The influence of relative humidity on light sensitivity is controversial, it is usually accepted that a high humidity increases the light sensitivity, Figure 6, however more sensitivity at low relative humidity, after elimination of the dark reaction effect, has been claimed by some researchers (12).

Light Sensitivity Enhancement

Additives to dichromated colloids can increase the light sensitivity but always at a cost in keeping properties by acceleration of the dark effect, 0.1% cupric chloride, for example, increases the sentivity three to four times but with a

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shelf life decreased accordingly. Despite repeated efforts no satisfactory solution has been found to the low printing speeds. It must be noted that methylene blue and other dyes can be used to broaden the spectral sensitivity over the entire visible range, Figure 7. The blue peak is due to the dichromate and the red peak to the methylene blue. Note that a He-Ne laser would be very effective for direct pattern generation.

PRACTICAL INDIRECT-DIRECT SCREEN MANUFACTURE

Materials

Using the data reviewed to this point it is clear that the manufacture of the screens can be optimized for good keeping properties and light sensitivity by the choice of the nature of the colloid (polyvinyl alcohol), the dichromate (ammonium dichromate), the temperature (low) and the pH (high) and possibly a compromise with light sensitivity additives.

Several commercially offered systems were tried including indirect-direct diazo sensitized systems and direct emulsions. Chromaline [13] type B-100 along with the direct fluid emulsion type A1 and Chromaline bichromated sensitizer proved to be the best all around performers. These materials are commonly available at low cost since they are widely used in silk-screen printing.

Emulsion Mounting

Two methods are used to mount indirect-direct emulsions on screens and sensitize them. The 'dry process' consists in mounting the emulsion and drying it with no sensitization at this stage. The 'wet process' requires mounting the emulsion and sensitization simultaneously. With all types of emulsion consistantly better results were obtained with the dry process in our experience. The emulsion film together with its support film are quickly dipped in clean water and promptly layed flat on the pre-wetted clean screen mesh. The screens have, of course, been thoroughly degreased after tensioning. No motion mesh to emulsion must occur and an even low pressure stroke with a rounded soft squeegee eliminates the excess water. A cabinet with 35°C warm air circulation is used to dry the emulsion. As soon as the emulsion is dry, one can proceed to the sensitization, or build-up several alyers, an extremely useful technique if large thickness deposits are required as for solder-paste screens. For multilayer work the plastic support film must be removed and a new emulsion layer is placed as before. Care and some dexterity are required to obtain consistent results; however one can practice as often as necessary by merely washing the screen and starting over until the necessary skill is acquired.

Sensitization

The colloid and its sensitizer are mixed according to instructions avoiding air trapping when mixing. Not all polyvinyl alcohols and sensitizers are equal as supplied from different manufacturers, the better ones control the pH with additives. The small cost involved does not warrant developing your own system but choosing the proper commercially available materials is essential. After removal of the plastic backing on the emulsion a thin layer of sensitized colloid is deposited on the squeegee side of the screen with a single stroke of a direct

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emulsion scoop. The screen is then put back in the drying cabinet. In case of several emulsion layers, routinely up to six, enough colloid must be supplied to sensitize completely through the thick previously dried layers without soaking them to destruction. A few trials will quickly guide the operator.

Exposure

A plexiglass exposure frame can shorten the exposure times as indicated in Figure 9. Many light sources are available for efficient exposures, Figure 10. The correct exposure can be determined with step tablets or by critical examination of resolution targets, optimizing for the best details possible in the target. Depending on the screen mesh size, lines of 1 to 2 mils width on 1 to 2 mils spacing can be obtained routinely, hence the material resolution is not the limiting factor in the printing process. Figure 11 shows a 1 mil layer on a 350 mesh screen. The resolution and the adhesion mechanism to the wire are clearly visible. Multilayer emulsion screens require increased exposure to penetrate through the thick layer. A small decrease in resolution is to be expected; however since these are usually used in combination with coarse screens this is not a limiting factor as evidenced in Figure 12. Screens which are still chilled from storage, as shown below, can be exposed with a corresponding increase in exposure time.

Storage

Immediately after sensitization and drying the screens can be stored in a freezer or the freezing compartment of a refrigerator. No degradation in screen properties are observed after two month storage at -5°C therefore screens can be prepared at a convenient time and put away for future use. Exposure immediately after storage is possible thus durable screens can be produced on extremely short notice if needed. The screens can also be prepared by larger batches to save time and exposed as the need occurs. This convenience is available from commercial screen manufacturers (diazo emulsions), however these do not offer control over the emulsion thickness and are more costly as expected.

Development

The image development is done by soaking in warm water (45 to 50°C) for five minutes followed by gentle spray of warm water on the printing side to clear the residual colloid. Additional soak in clean 45-50°C water for two minutes terminates the development. Drying is done by blowing dry compressed air or nitrogen from the substrate side. A few minutes in a stream of air completes the drying.

Reclamation

Despite some attempts with chlorine solutions and ultrasonic baths no satisfactory method has been found to reclaim the screens, however due to the long life of the layer reclamation would be futile in many cases since the screen has lost its original properties by wear.

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CONCLUSION

A fast preparation method of long-life screens has been presented using indirect-direct emulsion sensitized with a dichromated colloid at the operator's convenience. This is possible because of freeze storage of these screens. Thick layers are obtained for special applications without the use of metal-mask screens. A little practice is necessary to prepare these multilayer emulsion screens but no special equipment is required as opposed to metallic stencils.

JJHR:lg
December 1, 1976.

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TABLE 1 MAIN ORGANIC COLLOIDS USED IN PHOTOMECHANICAL PRINTING

Natural Organic Colloids

Gelatin	Casein
Fish Glue	Gum Arabic
Egg - Albumin	Shellac
Blood - Albumin	Zein (protein from corn)

Starch (corn, rice, tapioca, wheat, potato)

Synthetic Organic Colloids

Nitrocellulose
Cellulose acetate phtalate
Cellulose acetate citrate
Cellulose acetate succinate
Sodium carboxyl cellulose
Polyvinyl - pryyolidone
Polyvinyl butyrol
Halogenated polyvinyl alcohol
Urea - Formaldehyde Resins
Vinyl Methyl Ether

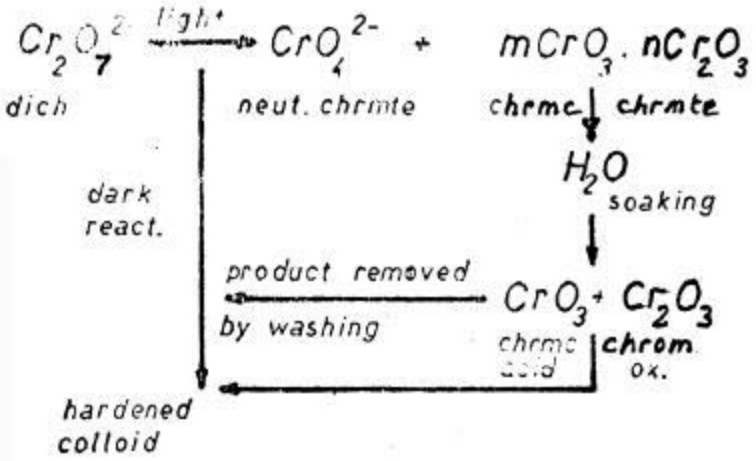

FIGURE 1 Simplified photochemical reaction of a dichromated colloid.

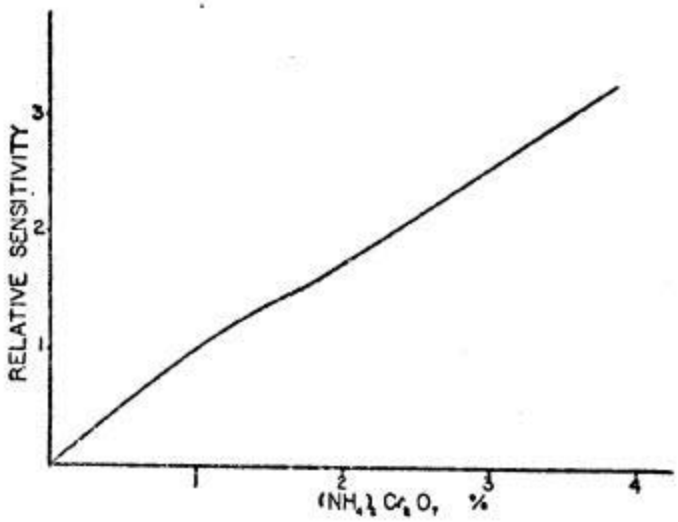

FIGURE 2 Relation between the concentration of a dichromate and the sensitivity to light of the dichromated colloid.

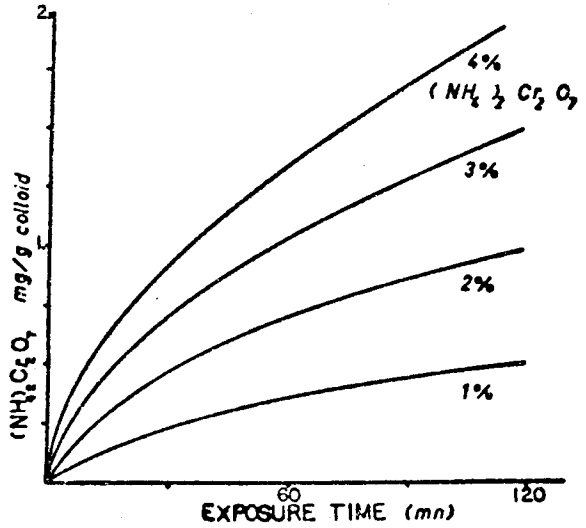

FIGURE 3 Relation between hardened product of exposure of dichromated colloids and time.

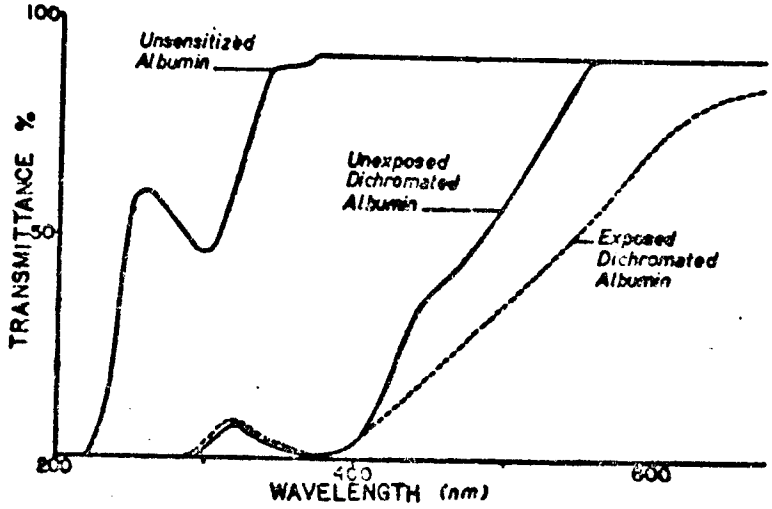

FIGURE 4 Tranmittance of a typical dichromated colloid.

DARK REACTION

$$Cr_2O_7^{2-} + 6\,H^+ \rightarrow Cr^{3+} + CrO^{2-} + 3\,H_2O$$

chromic ion green; chromate yellow; decreases viscosity

FIGURE 5 Simplified dark reaction.

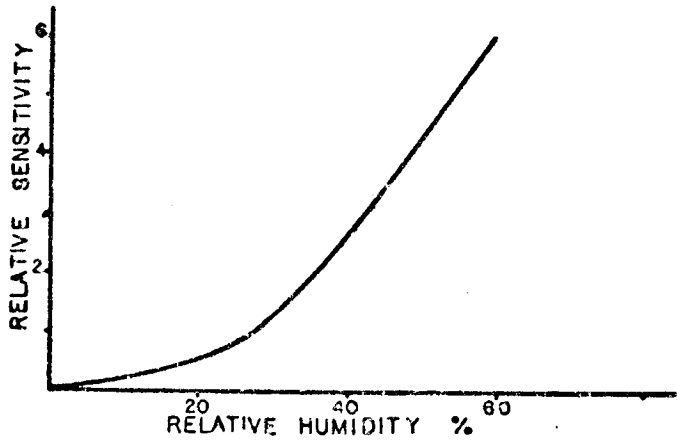

FIGURE 6 Effective relation between the sensitivity of a dichromated colloid and the relative humidity.

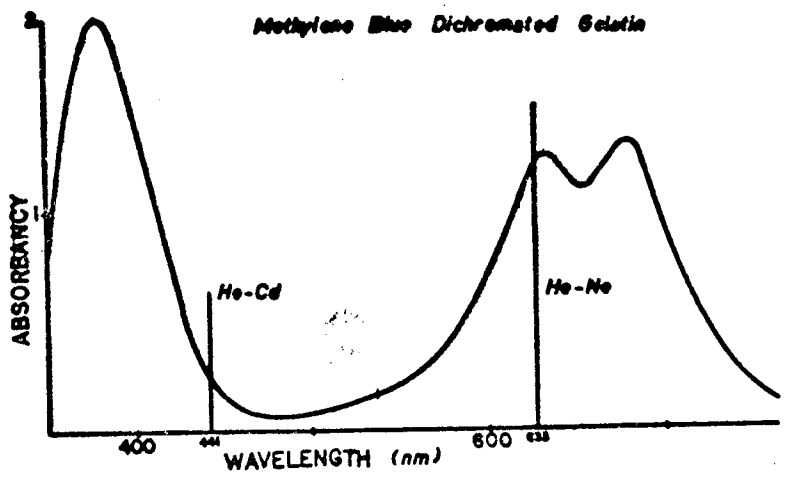

FIGURE 7 Dichromated gelatin spectral sensitivity after addition of 1×10^{-3} mol/liter methylene blue.

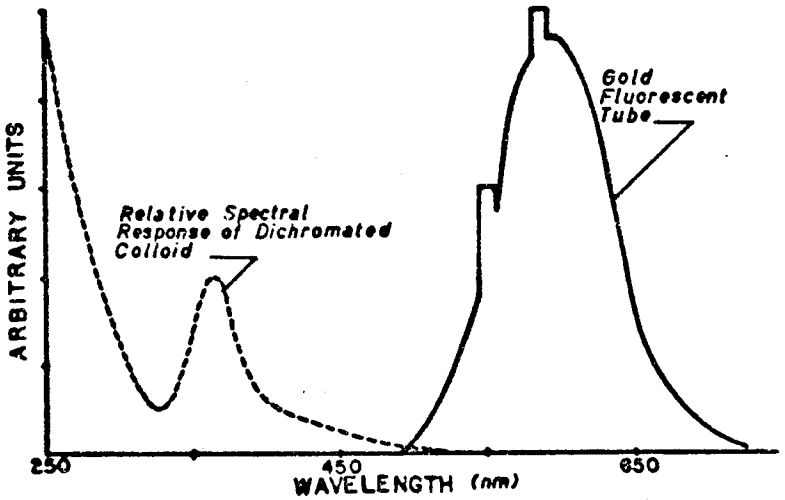

FIGURE 8 Spectral emission of a gold fluorescent tube. The slight overlap within the 500 mm region can cause eventual fogging or scumming of the emulsion after prlonged exposure.

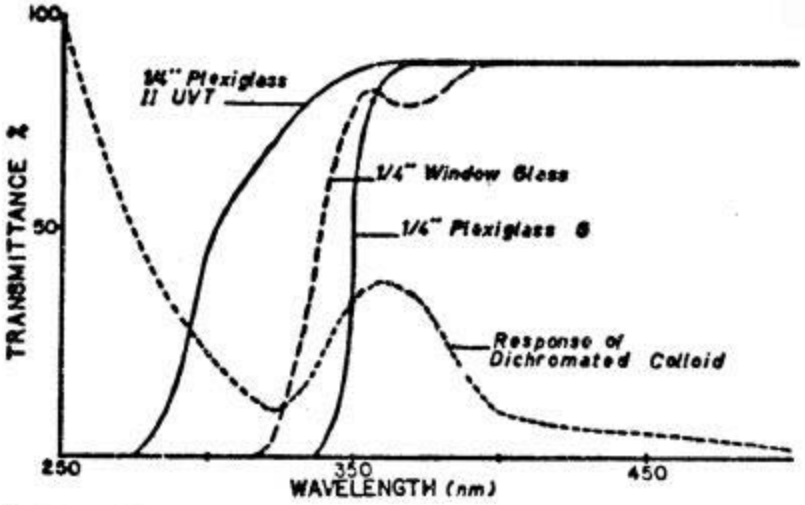

FIGURE 9 Transmittance of materials available for construction of exposure frames.

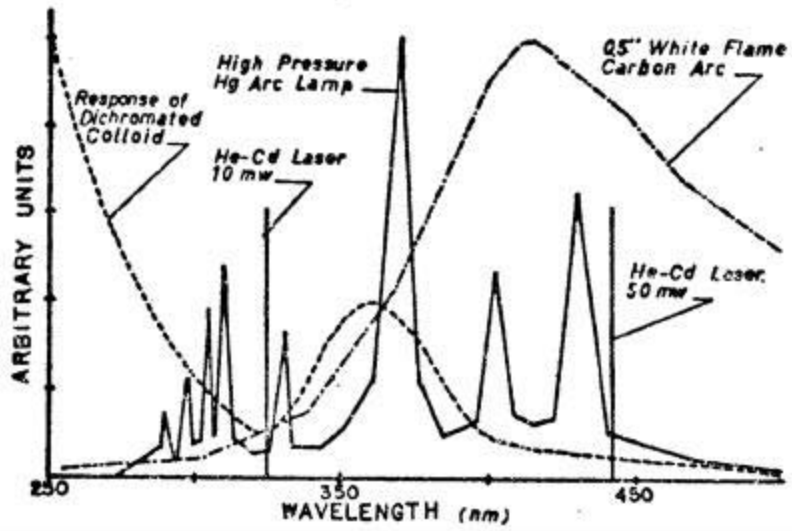

FIGURE 10 Spectral emission of several suitable sources for exposure of dichromated colloids.

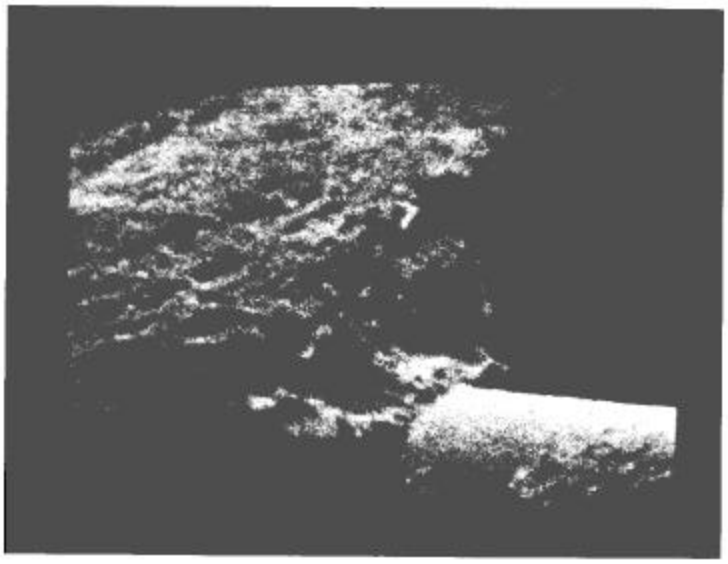

FIGURE 11 1 mil emulsion on 350 mesh screen. The wire size is approximately 1.05 mil diameter.

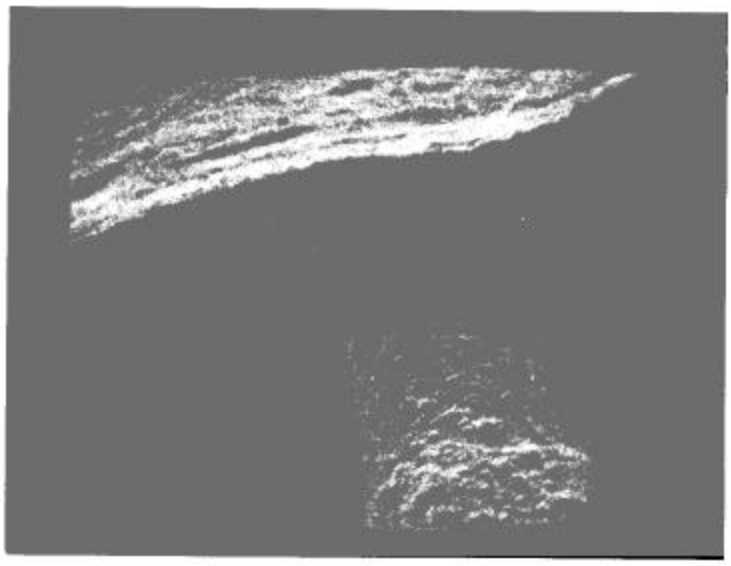

FIGURE 12 3 layers (3 times 1 mil nominal) and the dichromated colloid adhesion layer are visible on these SEM pictures of an 80 mesh screen. The wire size is 3.75 mil diameter.