KENNEY & ROSS LIMITED

R.R. # 3 SHELBURNE, NOVA SCOTIA CANADA B0T 1W0
PHONE: (902) 637-2616 FAX: (902) 637-2511

Photoengraving Glue

Introduction

Although fish gelatin has been used in commercial processes since 1890, few people are aware that there exists any other type of gelatin but animal. Both are obtained from a similar source — the skin. With animal gelatin, the usual source is the hide of cattle, although gelatin may be obtained from the skin of any other animal where sufficient quantities are to be found. With fish gelatin, the usual source is from the cod.

Chemically speaking, both types of gelatin have the same 20 basic chemical constituents. However, the proportions of these chemical constituents differ, depending upon the source, whether the source be fish or animal, or different species of fish or animal. The main difference between fish and animal gelatin is that a water solution of fish gelatin is a liquid at room temperature, whereas a water solution of an animal gelatin is a solid. Both gelatins have other properties that are similar. They can be used as high strength glues (fish glue and hide glue). They make excellent bases for emulsions, and they can be made light sensitive by the addition of sensitizers, thereby finding use in photographic processes.

Fish gelatin has been known since 1890 as photoengravers glue. Photoengraving glue can be obtained in various degrees of purity, the gelatin grade being crystal clear. Since fish gelatin (or fish glue) is a liquid at room temperature, it is easy to handle as a coating. Chromium salts (such as ammonium bichromate, potassium bichromate, or ammonium chromate) can be added in varying proportions to make the gelatin sensitive to light. Exposure to light (especially actinic rays from an ultraviolet lamp source or from sun light) will insolubilize the gelatin, although the exact reaction is still not fully understood by chemists.

The use of photoengraving glue in a photo resist is based principally on the adaption of these properties; fish gelatin solutions can be made light sensitive, are easy to use as coatings, and upon drying these coatings can be insolubilize with light. Further baking will convert the coating into an acid resistant polymer.

Chemistry

Fish gelatin is a protein molecule consisting of a complex chain of 20 amino acids. The molecular weight of fish gelatin (or photoengraving glue) is estimated to be between 30,000 and 60,000. The specific properties of the molecule are dependent upon its molecular chain length and the reactive end groups that are on the molecule. These reactive groups are hydroxyl (OH), carboxyl (COOH), and amino (NH2).
The photo hardening of dichromated colloid layers has been studied at some length over the past years. The literature contains considerable reference to various explanations. We would suggest the photo hardening to be the result of an oxidation-reduction reaction that is accelerated by light in the ultraviolet wave length range. The oxidation-reduction equation for bichromate is as follows:

$$Cr_2O_7 -- + 14H^{+} + 6e \quad 2Cr^{+++} + 7H_2O$$

Under the action of light, the colloid is oxidized by the bichromate, and trivalent chromium is formed. Since trivalent metal ions will gel a colloid, the resultant areas exposed to light will not wash away when the colloid layer is rinsed with water.
The sensitivity of the coating is dependent upon these factors:
1. The composition of the coating.
The coating composition requires a colloid that reacts with bichromate under ultraviolet light and cross links with resultant trivalent chromium to form a gel.

2. The thickness of the coating.
Since the light must penetrate and insolubilize the coating to the interface of the surface coated, the thickness is important. Otherwise there will be no adhesion.

3. The distance of the light from the coating.
This determines intensity at the photo resist surface.

4. The wave length of the light source.
The light source must have the proper wave length that is absorbed by the photo resist.

5. The time of exposure.
The time of exposure (together with intensity) determine the total light energy.

In forming a dichromated colloid image on a metal surface, it is necessary to obtain a gelled image that will not readily wash away. Insufficient exposure will result in insufficient trivalent ions being formed. The resultant image will not form a hard gel but will swell and sluff off when washed with water. Sufficient exposure must be made so the image will not swell excessively upon washing, and then will dry down to a glossy coat.

The ratio of bichromate to colloid will also affect the sensitivity. For photoengraving glue, the ratio can be varied from 1 part ammonium bichromate/ 20 parts liquid glue (by weight as supplied) to 1 part ammonium bichromate/ 7 parts liquid glue. The sensitivity will increase as the bichromate concentration is increased, reaching a peak at about 1 part ammonium bichromate/ 10 parts liquid glue weight. Additional bichromate concentration will reduce the sensitivity, because the light will not penetrate the coating as deeply.

Only a small percentage of the bichromate reacts with the colloid. The remainder is washed out during the image development step. However, the excess amount is necessary to obtain the proper sensitivity.

General Properties of Photoengraving Glue

Photoengraving Glue is supplied at a 45% solids solution with a viscosity in the range of 4000-5000 centipoise, or similar to honey. The glue as supplied is protected with a bactericidal agent that will give it a long shelf life. Preferred storage temperature is 75°F (24°C) or less, away from exposure to heat or direct sunlight.

Like all colloid solutions, the viscosity is dependent upon temperature. Photoengraving glue becomes more viscous as the temperature is reduced, and will form a gel at temperatures below 50°F (10°C). If the cold or gelled glue is heated to room temperature, the viscosity will return to normal with no chemical change. If the glue arrives frozen or gelled because of winter temperatures, store at room temperature for a day before use so that it can be poured out of the container.
Photoengraving glue is a protein that is an excellent food for bacteria. The glue as supplied is protected. Diluting will reduce the effectiveness of the preservative, and non sterile water will provide the bacteria culture necessary to start a vigorous growth within a few days. The addition of bichromate will act as a preservative and effectively stop any bacterial action. The above is pointed out so that the user will not pre-dilute large quantities of photoengraving glue. Dilute only enough to make the photo resist.

Mixing of Resist

To make a photo resist, photoengraving glue must be diluted with water to give the proper coating viscosity. Sensitizer is then added, with any additional ingredients which are described further on.

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Here is a good starting formula:

Photoengraving glue	27%
Water (preferable de-ionized)	70.3%
Ammonium bichromate (technical grade)	2.7%

To mix, dilute the glue with water using stirrer. Add the ammonium bichromate, and allow enough time for the mixture to dissolve the bichromate while stirring.

The above formula is based on weight percentages, and will give a total solids of approximately 15%. This viscosity range will be 10-12 centipoise. This is a good range for either whirler coating or dip coating.

The PH of the photo resist will be 5.5-5.6. The solution will have a shelf life of 4-7 days depending upon the storage temperature. A temperature of 65-70ºF (18-20ºC) is generally preferred. Higher temperatures will reduce the shelf life.

The photo resist should be filtered before use, and allowed to stand to remove air bubbles. We use a 5 micron cartridge filter which gives excellent results. If finer filtration is required, micro porous filters are available to remove particles as small as 1 micron.

Store the photo resist in a stainless steel container, or a dark plastic container, away from bright light. The photo resist is not very sensitive to visible light, but preferably should be handled in yellow light.

The amount of water added can be varied, to give a particular viscosity for a specific coating procedure. Although a heavier coating will offer more acid resistance, more light is required to insolubilize a thick coating. In most cases a thin coating gives adequate resistance.
With any bichromated colloid solution, there is a possibility of limited shelf life because of the "dark reaction" between the bichromate and the colloid. Temperature, concentration of the bichromate, concentration of the colloid, and pH all affect the dark reaction. The viscosity will gradually increase and the mixture becomes progressively more light sensitive. Eventually the coating will not wash away cleanly and will leave a scum on open areas that should be absolutely clean.

It is possible to increase the shelf life by neutralizing the mixture to a pH of 6.8-7.0 with ammonium hydroxide. Sensitivity of the mixture will be reduced, but the shelf life will be greatly extended to a month at least. Do not use any other alkaline material in place of ammonium hydroxide.
If additional sensitivity is required, we recommend adding dilute sulfuric acid to the original formula and reducing the pH to 5.0. This will decrease the printing time and also decrease the shelf life. Use a 5-10 percent solution of sulfuric acid and add it slowly to the photo resist while it is being stirred.

Cleaning the Surface to be Coated

To obtain maximum adhesion of the photo resist, the metal surface must be chemically clean and water wettable. Either one or a combination of the following methods can be used:

1: Abrasion - using a pad with or without pumice
2: Soaking the sheet in a water based cleaning agent
(usually at high temperatures).
3: Electrolytic cleaning.
4: Pre-etching with an etchant.

We do not recommend vapor degassing except to remove excessive amounts of oil before one of the above steps. Some of the above methods will change the surface finish of the metal. The specific surface requirements of the finished part may well determine the cleaning method used

A good way to test the cleanliness of the sheet is to wet with water and then drain. The surface should hold a film of water for at least 30 seconds and preferably one minute, without the formation of voids.

Most metal cleaning agents are alkaline. If an alkaline cleaner is used, the cleaned sheet should be dipped into a dilute acid solution (5% nitric acid) then rinsed. The photo resist will have poorer adhesion to an alkaline surface, and so such a surface should be neutralized. We recommend a final rinse with a deionized water after any cleaning step. If drying is necessary, dry in a clean atmosphere. Either room temperature drying or oven drying can be used. Water based photo resists have excellent adhesion to clean metal with a water wettable surface. If the photo resist flakes off during drying or the later post bake step, the metal has not cleaned properly.

Sometimes the method of cleaning will affect the surface of the metal and reduce the rate of etching. If you use a chemical or electrolytic cleaning method, compare it initially against the abrasion method. Clean separate pieces of metal by each cleaning method, and then immerse the cleaned metal in the etchant. The metal cleaned by abrasion with pumice should etch readily. The metal cleaned by the other method should etch just as readily, but if it does not, check the chemicals used to determine what is leaving residual deposits.

COATING OF THE PHOTO RESIST

On most continuous in-line production equipment, the water based photo resist is flow coated onto the wet strip, displacing the rinse water from the metal. For dip coating of single sheets, the metal to be coated should be dry. Note that trace amounts of moisture can be tolerated.
For dip coating, the speed of withdrawal will determine the coating thickness. A slow withdrawal speed (4-6 inches per minute) will give an acceptable coat with the photo resist formulation supplied. A faster withdrawal (up to 12 inches per minute) will provide a thicker coating but will also take longer to dry and to expose or print. Drying time will be 5-15 minutes at 150 ° F
(65 ° C). At the higher speeds, the coating thickness will be greater at the bottom than at the top,
because of the run off of the photo resist. The slower speed will give a coating thickness of 2.5 to 3 microns. The higher speed will give a coating up to 5 microns.

Too thin a coating thickness will show as an iridescent fringe on the top of the coated sheet. This is more apt to happen on a very smooth and glossy metal surface. If the coating thickness is to thin, the photo resist will break down prematurely during the etching cycle.

In any coating operation, steps should be taken to eliminate bubbles. Any violent mixing or pouring of the photo resist may result in an air bubble forming. In dip coating, these will be attracted to the metal sheet as it is withdrawn and result in a coating flaw. Careful control of any pumping or circulating device will keep the bubbles to a minimum. When starting to dip coat, the first plates will generally clean out any residual bubbles that are in the tank.

DRYING OF THE PHOTO RESIST

As mentioned before, a drying time of 5-15 minutes at 150 ° F (65 ° C) is usually sufficient. A lower temperature can be used, and the sheet can be checked for dryness by touching a bottom corner.
Too high a temperature can heat fog the resist. High temperatures accelerate the sensitizer in the resist, causing the coating to go blind. The printed image will not develop.

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Either convection heat or infra red heat can be used. A wet bead on the bottom of the sheet after drying can be wiped off, or cut off. Longer drying time will also eliminate the wet bead, and a temperature of 150 ° F or less will not harm the resist.

EXPOSURE

The light energy to insolubilize the resist film is much greater than that required for silver halide photography. Light in the yellow wave length will have little effect on the resist film. Ultra violet wave length has the most effect, with maximum absorption in the 3200-3800 angstrom wave length.
Time of exposure is dependent upon the source of light and distance between the resist coating and light. Here are some examples of exposure times for a coating thickness of standard sensitivity.

Light Source	Distance	Time
15 amp single arc	15 inches	6 minutes
95 amp single arc	48 inches	4 minutes
4500 watt pulsed xenon	36 inches	4 minutes
8000 watt pulsed xenon	10 inches	30-45 seconds

Reducing the distance or increasing the time will both increase the amount of exposure. Cutting the distance in half will have the same effect as quadrupling the exposure time.
Exposure is carried out using a vacuum frame which will draw the negative in close contact to the resist film. The emulsion side of the negative should be next to the coated sheet, to provide absolute contact of the print to the resist.

The density of the negative is very important. Lines black to the eye may be translucent to the light source, and the lamp will print through the negative where the lines are supposed to block out the light.

DEVELOPMENT OF THE PHOTO RESIST

The exposed image is next washed with room temperature water. The unexposed portions will wash out quickly and completely. This feature makes the water based system very safe to handle. It eliminates the cost, handling, storage and disposal of hazardous solvents.

Long washing periods are not necessary. The image should wash clean in a minute, less if a fine spray is used. In using a spray, normal water line pressure is adequate, but this should be controlled if there is any large fluctuation. A water temperature of 75-85 ° F (24-29 ° C) is recommended. Although temperatures up to 100 ° F (38 ° C) are used, we would avoid any water temperature in excess of this. Too high a temperature can swell the resist image.

If it is desired to visually inspect the image, it can be dyed with a water soluble dye. Use 5 grams of water soluble methyl violet dye in a gallon of water. Immerse the developed sheet in the dye solution for 15-20 seconds, remove and rinse with tap water.

To dry, the sheet may be blown dry with a stream of compressed air, whirled dry or allowed to dry in war air.

BURN-IN

To obtain acid resistance, the image must be baked at a temperature of 500-550 ° F for 5-10 minutes. This is best done in a heated oven, as the polymerization is the result of an oxidation step and requires air. One word of caution is necessary. Do not develop the image and place it wet into the hot oven. The sudden expansion of steam will

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blister the photo resist and reduce the acid resistance of the image. The wet image must be dried before it is placed in the burn-in oven. In an in-line operation where a continuous sheet is being processed, it is possible to go from the developing step into the hot oven. This is because the air between the two stations is heated by the circulating air escaping from the oven. The wet photo resist is thus dried before it enters the hot oven.

The high temperature bake will darken the photo image and give an indication of the extent of polymerization. Such factors as color of the metal and thickness of the resist also affect the apparent color of the image, but once the proper conditions are determined, the check can be visual. The color should be between tan and a light brown. Too light a color will show insufficient polymerization. A color approaching black will show too high a temperature resulting in charring and breakdown of the photo resist. Either of these conditions is caused by temperatures outside the 500-550 ° F range (260-288 ° C).

We have found that as the time of bake is increased, the acid resistance increases until it reaches a plateau. The higher temperature (550 ° F or 288 ° C) will give somewhat better acid resistance and will likewise be more difficult to remove.

A temperature lower than 500 degrees F for a longer time will not polymerize the resist. A temperature of at least 500 ° F (260 ° C) is necessary.

ETCHING SOLUTION

Ferric chloride is the preferred etchant for metals commonly processed. The best etching characteristics are obtained using 48 degree Baume ferric chloride at 120 ° F (49 ° C). Speed of this etchant can be increased by raising the temperature up to 170 ° F (77 ° C). Faster etching speeds are obtained by using the more dilute 42 degree Baume ferric chloride. However, a more ragged edge is obtained on many metals.

STRIPPING

After etching, the resist can be readily dissolved and thoroughly stripped by immersing the sheet for 30-60 seconds in a 5-10% water solution of caustic soda (sodium hydroxide) heated to 160-180 ° F (72-82 ° C). Care should be taken so that the caustic is not splashed on the skin or in the eyes.

STAFETY PRECAUTIONS

Although bichromates, acids, and alkalies are used in many production processes every day, we wish to point out that care should be exercised to avoid contact of these materials with the skin and eyes. A good safety procedure is to use rubber gloves and rubber apron when handling these materials and safety goggles when there may be danger of splashing.
Photoengraving glue is non-toxic by itself, but the bichromate resist should be handled in such a manner as to avoid undue skin contact.