lose gum. The gum solution is usually only gum arabic and water, or acidified cellulose gum and water. The etch is usually more acid than the gum. The pH of an etch is usually in the range of 2.0 to 3.0 while the pH of a gum solution is usually about 4.0-4.5.

Requirements of a Desensitizing Gum. The gum in the etch or gum solution must fulfill two functions. It must be the type of material which is water-loving or "hydrophilic" so it will prefer water rather than ink on the press. Secondly, it must hold tightly to the surface of the metal in the non-image areas. The plate is wet continuously by the water fountain solution on the press. If the gum dissolved rapidly from the plate, the bare metal would soon be exposed and might begin to take ink. Many natural and synthetic materials are hydrophilic and thus fulfill the first requirement. Some of these are gum tragacanth, gum arabic, cherry gum, larch gum, mesquite gum, methyl cellulose, hydroxyethylcellulose, arabogalactan, dextrins, alginates, oxidized starches, polyvinyl pyrrolidone, and polyvinyl alcohol. But these materials vary widely in their ability to adhere well to a metal surface and therefore differ widely in their efficiency in desensitizing the non-image areas of a lithographic plate.

Probably these desensitizing materials do not actually react chemically with the metal, but are *adsorbed* on the surface of the metal (see page 109). A good desensitizing gum such as gum arabic is very soluble in water. When a pressman "washes off the gum" when he starts a plate on the press, he removes a considerable amount of the gum which has been dried on the non-image areas of the plate. But a thin, adsorbed film of gum remains attached to the metal. This adsorbed film cannot be removed with water and it is this film which desensitizes the non-image areas.

Why Some Materials Desensitize Better Than Others. There are still things to be learned as to why certain materials desensitize a plate at all and why some of them are better than others. In the first place, the material must be water-loving or "hydrophilic." Most of the materials which are used in lithography are water-soluble, organic materials which contain hydroxyl groups (—OH) in their molecules. So it may be that these hydroxyl groups are at least partly responsible for the hydrophilic nature of these desensitizing materials.

When the good desensitizing agents are examined, it is found that most of them are salts of high molecular weight, weak organic acids. Thus gum arabic is a mixture of the calcium, potassium, and

magnesium salts of "arabic acid." Cellulose gum can be classed as the sodium salt of a high molecular weight, weak organic acid.

In the chapter on Chemistry of the Compounds of Carbon (page 87) you learned that many organic acids have the general formula R—COOH. The letter "R" stands for an organic radical, such as $-CH_3$, $-C_{15}H_{31}$, etc. The —COOH group is called a "carboxyl" group, and is present in all organic acids. When the hydrogen atom of the carboxyl group is replaced with an atom of a metal, a salt of the organic acid is formed. Thus the salt, sodium acetate, can be written $CH_3—COONa$.

The reason we are reviewing this material on organic acids and their salts is that it is fairly certain that the carboxyl groups which are present in good desensitizing agents are responsible for the adsorption of these agents to the surface of the metal. It is thought that the —COOH groups adhere tightly to the metal surface and thus the whole molecule, of which the —COOH groups are a part, is held to the metal.

Other groups than carboxyl groups may help to hold a desensitizing agent to a metal surface. For example, Irish moss was found to be a fairly good desensitizing agent (LTF *Research Progress* No. 20, Feb., 1951) but is not supposed to have any carboxyl groups in its molecules. But the fact that hydrophilic materials such as starch, dextrin, and methyl cellulose are poor desensitizing agents is attributed to the absence of carboxyl groups in their molecules. And other materials which have desensitizing properties, such as sodium starch glycolate and the alginates, do have carboxyl groups in their molecules. The alginates are sodium, potassium, or ammonium salts of a weak organic acid called alginic acid.

Why Desensitizing Etches Are Acidified. It is well known that good desensitizing agents such as gum arabic or cellulose gum do a better job of desensitization when their water solutions are acidified, usually with phosphoric acid. The acid converts the "salt form" of the gum into the "free acid form." That is, a group like —COOK ("salt form") is converted into —COOH ("free acid form"). For example, one of the molecules present in gum arabic may be written XCOOK where "X" stands for a large number of carbon, hydrogen, and oxygen atoms. When a gum arabic solution is acidified with phosphoric acid, the following reaction occurs:

$$\underset{\text{salt form}}{XCOOK} + H_3PO_4 = \underset{\text{free acid form}}{XCOOH} + KH_2PO_4$$