Since experience has shown that an acidified gum arabic solution desensitizes better than one with no acid, it can be assumed that the —COOH group gives a better adsorption bond to a metal surface than a group like—COOK. For further proof of this one can go to alkaline solutions of gum arabic. If a solution of gum arabic is made alkaline with, say, ammonium hydroxide, all of the —COOH groups are converted to $-COONH_4$ groups. Such an alkaline solution of gum arabic is a very poor desensitizing agent, at least on zinc plates.

Effect of pH on Desensitization. The following discussion is concerned mostly with the desensitization of zinc litho plates. If the pH of the desensitizing etch is on the alkaline side or as low as 6.0, most of the gum arabic or cellulose gum is in the "salt form." Because of this, the desensitization is poor.

As more phosphoric acid is added to the etch solution, to bring the pH down to 5.0, 4.0, and 3.0, the etch becomes a better and better desensitizing agent. What is happening is that more and more of the "salt form" of the gum is being converted to the "free acid form."

At a pH of about 3.0 most of the gum has been converted to the "free acid form," and the desensitizing powers of the etch are very good.

Up to now there is very little free phosphoric acid in the etch solution. It is true that phosphoric acid has been added to the etch solution, but it has reacted chemically with the gum to convert the gum to its "free acid form." When the pH gets down to about 3.0, most of the gum has been converted to the "free acid form." If still more phosphoric acid is added to the etch solution, there is nothing for it to react with and it remains in the etch solution as free phosphoric acid. This free, or excess, phosphoric acid then begins to attack the surface of the zinc plate. This makes it more difficult for the gum to become adsorbed onto the zinc and the desensitization becomes poorer again. It is well known that a gum arabic etch which is too acid acts as a "counter-etch" instead of an "etch." It "sensitizes" the plate instead of "desensitizing" it. The reason for this has just been explained.

Here is a place where it is important to take a "middle ground" position. Up to a certain amount, the addition of acid improves the desensitizing etch. But much more than this amount makes the etch worse again.

Other Materials in Desensitizing Etches. The desensitizing gum is, of course, the most important material in a desensitizing

etch. Then we have just discussed the advantage of at least a certain amount of phosphoric acid in the etch. The role of other materials in desensitizing etches is still not too clear. Etch formulas often call for materials like ammonium bichromate, magnesium nitrate, zinc nitrate, ammonium nitrate, tannic acid, and chrome alum.

One possibility is that some of these materials may become adsorbed to the surface of the metal and alter the surface so that the desensitizing gum is adsorbed more tightly. This theory has never been proved.

Ammonium bichromate and nitrate salts such as magnesium or zinc nitrate are quite effective as corrosion inhibitors. For example, a solution of gum arabic and phosphoric acid of pH about 3.0 will react with a grained zinc surface with evolution of hydrogen gas. If enough ammonium bichromate is added to this solution, the evolution of hydrogen gas can be greatly reduced. Likewise, a solution of cellulose gum and phosphoric acid of pH about 3.0 will react with a grained zinc surface and hydrogen gas will be evolved. If enough magnesium nitrate is added to this solution, the evolution of hydrogen gas is practically stopped.

So, the addition of ammonium bichromate or a nitrate salt produces a desensitizing etch with more latitude as far as acid content is concerned. Enough acid can be used to convert practically all of the gum from its "salt form" to its "free acid form." At this point the etch has the best desensitizing power. If the etch contains enough ammonium bichromate or a nitrate salt, it will not attack the surface of the zinc plate even though the etch solution may contain a small amount of free phosphoric acid. This may be the principal reason for having these salts present in a desensitizing etch.

A desensitizing etch should be as simple as possible. No material should be included unless it can be proved that it does something to improve the adherence of the gum to the plate. It may be that a small amount of a chromic salt, such as chrome alum, will help to "harden" the gum arabic so it will not dissolve as easily from the plate and yet accept water preferentially. Such a material must be handled with care in an etch. If too much is present, it will harden the gum to such an extent that it will hold ink rather than water.

Change of pH of Etch on Zinc Plates. Even if a desensitizing etch is formulated at the right pH and contains a corrosion inhibitor such as ammonium bichromate, there is some chemical reaction with a zinc plate. It was found that the pH of a gum arabic-