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COMPOSITION FOR ETCHING AND ETCHING TRANSFERS

Nance Clayton-Kennedy, London, England

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This invention relates to compositions for carrying etching agents or colors and more particularly to compositions for etching glass and to the production of etching transfers.

The chemical etching of glass in the past has required the application of hydrofluoric acid or acid fluorides to the glass surface in liquid form. This has necessitated the use of stencils either in the form of perforated material impervious to the etching solution or compound or the coating of the glass with material such as paraffin wax over the portions which are to remain unetched. These procedures require a relatively large number of stencils due to the slow action of the etching solution or require considerable labor which adds to the final cost of the etched glass. Moreover it is relatively difficult to prepare stencils with very fine lines of shadings and finely etched designs have, therefore involved expensive hand work. It has also been proposed to apply fluorine compounds to glass by means of transfers printed on a collodion film, the etching being done by heating the glass in a furnace. Of course, the heating procedure requires rather elaborate equipment. No satisfactory etching compounds have been available, particularly for the production of fine designs or to produce transfers.

According to the present invention the etching is accomplished by means of an etching compound which is of such physical characteristics that it can be handled in much the same manner as embossing varnish or ink used for embossed printing or engraving. This composition is elastic and sufficiently quick-setting so that it may be printed or stenciled directly onto glass without spreading, or it may be printed onto suitable transfer paper from which transfer to glass may be effected by the simple action of moisture as will be described below.

The present invention, therefore, avoids all of the difficulties hitherto involved in stenciling glass with etching compositions. It is no longer necessary to maintain the stencil in contact with the glass until etching is completed, nor is there any tendency of the etching solution running under the edges of the stencil and blurring or spreading the pattern. It is also possible to print the etching compound directly onto glass and obtain sharp pattern outlines with no spreading or blurring and with a uniform depth of etching. The peculiar characteristics of the etching composition likewise permits the production of etching transfers. A product which has never hitherto been successfully produced and which, of course, permits a very cheap and effective etching without the complicated equipment required when the etching has to be done directly on the glass. The transfer method, which is nearly as simple as the transfer of colors to surfaces by the decalcomania process, opens up a new field for the etching of glass making the expert etcher's services unnecessary at the place of application. Transfers according to the present invention can be kept practically indefinitely in tight containers and can be produced at a high rate of speed by any suitable type of printing machinery.

The composition which makes the present invention possible is based on the discovery, that when a suitable soluble etching salt, such, as for example, an acid fluoride is disseminated throughout an elastic composition containing saccharides of the colloidal gelatinizing type mixed with gums having a plasticizing action on saccharides together with gums capable of forming a thick or tacky product, preferably with suitable fillers, a composition is produced which is highly elastic and can be applied to suitable printing surfaces such as engraved plates, stereo blocks, and the like, and will print clearly and evenly from the depressions of the block, either onto glass or transfer paper without smearing or sticking to the printing block.

While the choice of ingredients to be used in producing the composition permits considerable variation, care must be taken to obtain the proper consistency. This consistency will, of course, vary slightly with the nature of the printing operation and particularly with the humidity of the atmosphere where printing or transfer production is effected. The following detailed description of the preparation of the preferred composition of the present invention is illustrative of a typical composition, but it should be understood that the invention is not limited to the exact proportions and ingredients therein set forth and substitution of equivalents may be effected. The parts given in the formula are by volume.

A mixture is prepared containing one part of finely ground magnesium carbonate, one part of sugar, two and one-half parts of catechu or gum senegal, two parts of cornstarch, one part of semi-refined molasses, of the grade known to the trade as black or table treacle, and eighteen parts of water. The ground solids are mixed with the treacle and the water to assure complete dissemination and the mixture is boiled for one-half hour and allowed to cool. The cornstarch,

of course, imparts a jellylike consistency to the mixture. There is then added a mixture of one part of finely ground magnesium carbonate, one part gum tragacanth, two and one-half parts of cornstarch, twelve parts of acid ammonium fluoride ($NH_4F \cdot HF$) and one part of carbon black. The finely ground solids, after thorough mixing are stirred into the jelly of the first mixture until the entire mass is evenly distributed. Heat is then gradually applied, until the soluble constituents are dissolved and the mixture permitted to cool, whereupon one-half part of oil of rose geranium is added. For best results it is important after once cooling, no reheating of the mixture takes place.

A second mixture is formed of one part of finely ground magnesium carbonate, one part of ordinary sugar, four parts of gum tragacanth, with sufficient cold water to form a paste, a small amount of oil of rose geranium being added to permeate the mass. During stirring, the mixture changes in texture from a translucent to an opaque and grainy consistency which change requires several minutes of stirring. The two mixtures are kept separate, the first mixture keeps well for a week or two but then slowly deteriorates, requiring increased amounts of the second mixture to produce correct consistency, the second mixture can be stored practically indefinitely in airtight containers.

When printing or formation of transfers is to be effected, a sufficient amount of the second mixture is added to the first mixture so that a proper elasticity is produced and the composition prints clear from the printing block onto the glass or transfer paper as described below. The proportion of the second mixture which has to be added, will vary with the humidity of the air when printing, the age of the first mixture, and to a slight extent, with different batches. Assuming however, that a sufficient amount of the second mixture has been added to produce satisfactory printing, no further adjustment of the particular batch composition is necessary so long as the humidity remains constant.

The above formula and method of producing the two mixtures, I have found, gives best results but considerable variation in ingredients and some variation in proportions is permissible. Instead of magnesium carbonate, other finely ground, light, fluffy mineral fillers may be used. Care, however, must be taken when a filler other than a carbonate is employed, such as, for example, kieselguhr, as the magnesium carbonate is not entirely an inert filler even though this is its most important function, apparently some reaction with the fluoride takes place and compositions containing magnesium carbonate do not require quite as careful timing of etching and concentration of fluorides. Heavier carbonates such as ground barium carbonate may be used, but the resulting composition is less elastic and does not give quite as good results when printed rapidly.

The sugar can in general be substituted by other soluble carbohydrates which produce solutions of the same physical characteristics. Because of its cheapness, however, ordinary sugar is preferred.

The catechu or gum senegal which is an acacia product appears to have a solvent or homogenizing action on the carbohydrates and may be substituted by similar proportions of other gums having the same characteristics such as gum acacia. The cornstarch may, of course, be substituted by any other amylaceous product which swells with water to form a jelly of the same physical characteristics. The semi-refined molasses appears to contain some constituents which are not present in the lightly colored, highly refined molasses which is frequently sold for food purposes in the United States. When such molasses is used, the composition becomes soft and is not as reliable, on the other hand slightly more crude molasses may be employed successfully, even certain good grades of black strap molasses can be employed.

The gum tragacanth which is added with the fluoride appears to act as a thickener and prevents the compound from running when printing. Other gums having this same characteristic may be employed. It is significant to note that the action of heat affects the gum tragacanth, that is one of the reasons why the compound is stored in two forms which are mixed together just prior to using. The unheated gum in the second mixture, is not interchangeable with the heated gum in the first mixture. The proportions of heated and unheated gum may, however, be varied. In general because of the superior qualities of the unheated gum, as much should be present in the unheated state.

The fluoride to be used depends to some extent to conditions under which transfer or printing is to take place, and the character of the etching desired. In general the more soluble the fluoride the deeper will be the etching for a given exposure on the glass, but the greater will be the tendency for the lines to spread slightly, give up a softer edge to the lines and broadening them. The ammonium fluoride gives a quick etching action with a reasonable good definition. Where sharper, thinner lines are desired, part or all of the ammonium fluoride may be replaced by a less soluble fluoride such as sodium fluoride (NaFHF). The particular fluoride composition used will therefore depend on the character of the etching desired. It is possible, of course, to use compositions with different fluorides in different portions of the same print or transfer in order to produce very fine lines in certain portions of the design, and broader, softer lines in other parts. It is an advantage of the present invention that compositions can be prepared suitable for the most varied type of etching.

The carbon black performs the function of a soft coloring matter and may be replaced by any other soft pigment. Of course, a pigment should not be used which reacts with the other constituents and it might damage the composition. The rose geranium oil serves a double function, in the first place it inhibits the slightly unpleasant odor of the composition and the glycerine base acts as a smoother or plasticizer, very much better consistencies are obtained with its use. Of course, any other suitable plasticizer may be used if it is not of the oleaginous type, as oils tend to coat the fluoride particles or possibly the glass and thus produce uneven work. Glycerine base plasticizers have many of the solvent properties of water for inorganic salts and any such plasticizer may be used. The presence of the perfume is, of course, not essential to the operativeness of the invention, though some perfume is desirable where transfers are to be sold to the general public.

The application of the etching compound to a transfer or directly to the glass follows ordinary printing practice from blocks or plates with de-

pressed or engraved lines. Since, however, the composition is more gelatinous and elastic than the ordinary embossing or engraving ink, I have found that it is desirable, although not essential, slightly to bevel the edges of the lines or recesses in the printing block or plate. This aids in a clean separation of the composition from the printing block and results in uniform work of good definition. It is possible to print from unbeveled recesses if care is taken to maintain the optimum consistency of the composition. While the method of printing follows more or less standard practice, a typical application will be described in detail in connection with the production of etching transfers, a field in which the present invention is particularly important.

A plate is engraved with the desired pattern, the engraving tool being adjusted to give a slight bevel to the edges of the lines. The depth of engraving should be approximately $\frac{1}{16}$ of an inch, and a metal plate may be used, as the ordinary metals such as copper are practically unattacked by the etching composition. The composition is then forced into the lines either by spreading by hand and then wiping or shaving off the excess or by any of the well known mechanical means employed in embossed printing or engraving presses. Hand shaving or wiping should be at an acute angle to force the compound into all recesses. The plate is then applied to ordinary transfer tissue paper and the design prints clearly, leaving no residue sticking to the plate. Printing should be at moderate speed corresponding to ordinary engraving practice but due to the elasticity of the composition, the pressure employed may advantageously be somewhat increased. The printed design on the transfer tissue is in relief. Transfers can be kept indefinitely in airtight containers, but of course, should not be exposed to dry atmosphere for many hours, as this will result in drying out the moisture in the composition and will produce a crumbling or fissuring which interferes with proper etching, or if the atmosphere is very damp the compound may soften and spread.

In use, glass to be etched is moistened, the transfer firmly applied and the back of the transfer likewise moistened by pressing firmly with a damp cloth or other suitable means. The time required for etching will depend, of course, on the depth desired in the etched design and also to some extent on the solubility of the fluoride or fluorides used in the composition. For some designs from six to twelve minutes will suffice. After etching is complete, the transfer is removed and the glass carefully washed to remove the last traces of the etching compound. The fluoride employed is not strongly corrosive to the skin and the procedure, therefore, does not entail any particular hazard.

When direct printing on glass is necessary, the consistency of the compound may advantageously be somewhat more elastic and stiffer than when printing on transfer paper. The exact consistency will vary somewhat with the pressure employed and with the nature of the design, particularly the depth to which the etching is to be carried. The printed design on glass is moistened and remains for about the same time as in applying a transfer and then must be carefully washed off. Rapid printing is, however, possible as there is no tendency to smear during the period of etching. This is one of the great advantages of the present invention over the etching solutions employed in the past.

Where it is desired to stencil glass, any suitable type of stencilling machinery may be used, in general the stencilling presents no more problems than stencilling with ordinary varnish on a non-absorbent surface, thus for example: the glass may pass under a moving sheet of stencil which is pressed against the glass at one point by a roller covered with the composition of the present invention. The stencilled design does not tend to smear or creep and therefore, the stencil may immediately be removed from the glass and does not have to remain in contact therewith, for the period of time required for the composition to complete its etching action. This permits the use of high speed stencilling machines which have been entirely impossible with the etching compositions hitherto known. The present invention is not concerned with any particular type of stencilling machine and it is an advantage that it is applicable to a wide variety of standard machines, the only adjustments necessary being those of pressure and feed to handle the stiff elastic composition.

The invention has been described in detail in connection with the etching of glass by means of fluorine compounds. This is its most important field of usefulness in the present time, but it is not limited broadly to the etching of glass, any other material can be etched, provided the active etching agent is compatible with the carbohydrate-gum body of the composition. It should be understood that, broadly, the etching of any easily etched material is included in the invention, although in its more specific expectations it is especially concerned with the etching of glass.

The composition of the present invention may also be used for producing stencils for stenciling colors onto fabrics and similar surfaces by replacing the fluoride with a suitable coloring matter.

I claim:

1. A composition for etching glass comprising a fluorine containing compound capable of etching glass under the influence of moisture, dispersed through a carrier medium containing an amylaceous adhesive, a saccharide syrup of a consistency thicker than refined molasses, a mineral filler and an acacia gum and gum tragacanth in proportions such that the composition is sufficiently firm and elastic to print or transfer to glass without blurring during printing or during etching.

2. A composition according to claim 1 in which the mineral filler is a light, fluffy carbonate of an alkaline earth.

3. An etching composition for etching glass comprising an acid fluoride disseminated through a carrier medium consisting of cornstarch, black treacle, sugar syrup, gum senegal, gum tragacanth, carbon black, finely ground magnesium carbonate and a glycerine containing plasticizer, the proportions being such as to produce a composition sufficiently elastic and firm to permit printing or transfer to glass without blurring during the printing or for a sufficient period to permit etching.

4. A method of producing a composition according to claim 3 in which the sugar, black treacle, gum senegal, cornstarch and a portion of the magnesium carbonate are dissolved with sufficient heat to gelatinize the cornstarch, to which is added a further portion of finely ground magnesium carbonate, a small amount of gum tragacanth, a further portion of cornstarch, an

acid fluoride and carbon black, the whole being mixed to form an evenly distributed mass with the addition of a small amount of glycerine, producing a second mixture in the form of a paste of finely ground magnesium carbonate, sugar, unheated gum tragacanth and a small amount of glycerine, and mixing the two mixtures without heating just prior to use.

5. An etching composition for etching glass comprising a fluorine containing etching agent capable of etching under the influence of moisture, dispersed through a carrier medium sufficiently elastic and firm to print or transfer onto glass without blurring during printing or during etching under the influence of moisture, said medium containing carbohydrate adhesives, associated with at least one gum having a homogenizing action on the carbohydrate adhesive, and at least one gum adapted to give body to the composition.

6. An etching composition for etching glass comprising a fluorine containing etching agent capable of etching under the influence of moisture, dispersed through a carrier medium sufficiently elastic and firm to print or transfer onto glass without blurring during printing or during etching under the influence of moisture, said medium containing carbohydrate adhesives associated with at least one gum having a homogenizing action, at least one gum having a thickening action and a mineral filler, the carbohydrate adhesives including crude molasses.

NANCE CLAYTON-KENNEDY.