PROCESS FOR PREPARING PHOTOCONDUCTIVE COMPOSITIONS AND SHEETS COATED THEREWITH

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This is a continuation-in-part of my copending application Serial No. 44,871 filed July 25, 1960, now abandoned.

This invention relates to photoconductive compositions and sheets coated therewith, and to a process for preparing such compositions and making such sheets.

The aforesaid sheets consist essentially of paper or other suitable supporting means having on one side or both sides a photoconductive coating of an electrically insulating film-forming binder or vehicle in which zinc oxide or other suitable photoconductive substance is intimately mixed. In order to provide prints by the use of these sheets (which will hereinafter be referred to as photoconductive sheets), they are first charged upon their surfaces with a uniform electrostatic charge and the charged surface is then exposed to light through a photographic transparency or other indicia-bearing device. The portions of the surface upon which the rays of light impinge become discharged while the unexposed portions of the surface remain in charged condition. A colored powder mixed with finely divided iron filings is then brushed over the surface, whereby the powder is held electrostatically on the charged area. Surplus powder, including that on the uncharged areas, is brushed off and the remaining powder is fixed in position, as by heat, so that it will not be washed off or otherwise moved. Other methods for preparing the permanent print from the light-exposed sheet are also known.

The usual procedures for making photoconductive sheets comprise preparing a solution of the binder in a volatile organic solvent, incorporating the zinc oxide or other photoconductive substance into the binder solution, and then coating this composition onto the supporting sheet, followed by drying to volatilize the solvent. There are, however, many disadvantages in the use of volatile organic solvents, such as fire hazard, toxicity, and cost. While these disadvantages can be overcome to a considerable extent by the use of suitable ventilating means and solvent recovery equipment, such means and equipment introduce additional costs and operating problems which it is highly desirable to avoid if feasible. As a consequence, efforts have been made to replace the volatile organic solvents with water and thus to provide for dispersing the binder and the zinc oxide in the water to form the desired coating composition.

I have developed compositions of this type as exemplified in German Patent 958,355 issued February 2, 1957, to myself and Raymond Windfield James. Such compositions are prepared by dispersing zinc oxide in water, with the aid of a wetting or emulsifying agent, mixing the dispersion with a dispersion of binder (e.g., polyvinyl acetate) and plasticizer, and then spreading the resulting mixture on the base sheet and drying it. Other sequences of mixing may be used, but additives such as dispersants, emulsifiers, protective colloids and plasticizers have always been required with polyvinyl acetate or any of the other binders referred to, in order to provide a homogeneous mixture which could be spread by commonly used processes and apparatus and dried to form a film which had the desired flexibility as well as its photoconductive properties. The compositions and products disclosed in the aforesaid German patent are eminently suitable for uses and conditions where volatile solvents are to be avoided and where high humidity is not an important factor in the storage and use of the finished photoconductive sheets. I find, however, that high humidity conditions, especially humidities of 73% R.H. (relative humidity) and higher, have a deleterious effect on sheets so prepared. This is because the character of the coating is such that under the influence of such high humidity, the charge on the zinc oxide or other photoconductive substance is able to leak off. The sheets must be processed very quickly if legible prints are to be obtained, and even then the results are likely to be very poor or even indistinguishable. High humidity conditions of 75% R.H. and above are not confined to merely a few areas of the world, but are present for example throughout most of the densely populated eastern United States during the summers. The commercial importance of the humidity problem in the field of photoconductive sheets is thus obvious.

It is, therefore, an object of this invention to prepare photoconductive sheets which are suitable for use throughout the entire humidity range to provide satisfactory sharp prints. Another object is to provide photoconductive sheets by a process which does not require the use of volatile organic solvents, but in which water is used as the solvent or dispersing medium. Still another object is to prepare photoconductive sheets having coatings of which the binder for the photoconductive substance is of such a nature that it is especially effective to resist leakage of the charge under high humidity conditions. Other objects will appear from the accompanying disclosure.

It might be expected that the sensitivity to humidity of the photoconductive sheet would be diminished by avoiding entirely the use of water as a solvent or dispersing medium for the binder and reversion to the well-known though more costly and less convenient, organic solvent technique. On the contrary, however, I have found that I am able to use water as the solvent or dispersing medium and yet attain excellent humidity resistance by proper selection of a binder material and of suitable conditions of treatment, as described hereinafter.

The material of which the support for the photoconductive sheet is made must be conductive enough to permit leaking out of the charge developed in that portion of the surface film upon which the light falls. Paper is the material ordinarily used as this supporting material, but many other supporting materials known to this art may be used, particularly those of a cellulosic nature such as cellulose acetate, viscose, etc., in film form or made from fibers, e.g., by paper-making or by textile-making techniques.

In accordance with the present invention, I prepare a water-insoluble coating composition based upon a polymeric styrene-acrylate resin binder, finely divided zinc oxide as the photoconductive material, a styrene-maleic anhydride emulsifier and water. In achieving the final dried and cured coating all water and any water-soluble materials are either eliminated or converted into water-insoluble form. A water-insensitive coating, suitable for making good prints at a wide range of relative humidities and especially those above 75% is thus produced.
The styrene-acrylate resin binder is a copolymer of styrene and an acrylate, e.g., methyl acrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, ethylhexyl acrylate, etc., in the approximate ratio of 20% to 70% styrene, balanced acrylate. The particular acrylate selected in any given instance depends upon the qualities desired in the final film, more particularly the qualities of flexibility and softness. The use of amounts of styrene and acrylate outside of the foregoing range results in films which lack flexibility and softness and which may be discontinuous when applied.

Although the emulsion polymerization of styrene-acrylate resins is known, I have found that the resulting polymers obtained by usual commercial processes exhibit water-sensitivity and are not suited for the purposes of the present invention. However, by selecting an emulsifier that is not only compatible with the resin but actually reacts with the photoconductive material to produce an insoluble product, I have been able to overcome the problem of water-sensitivity. For this purpose, I use a styrene-maleic anhydride emulsifier in the presence of a volatile alkaline material whereby it is rendered soluble in water. The carboxy-containing groups of the styrene-maleic emulsifier react with the zinc oxide and are thereby deactivated or crosslinked. It may also additionally use a water-insoluble long chain fatty acid emulsifier such as stearic, oleic or palmitic acid although it is not necessary. A dispersant for the zinc oxide may also be used, if desired, but even if used the amount is so small as to be entirely insignificant in the final product.

It is a particular feature of this invention that instead of mixing the already polymerized styrene-acrylate copolymer with the photoconductive substance, I first mix the styrene and the acrylate monomers with the styrene-maleic anhydride and then polymerize the whole in situ. The carboxy-containing groups of the maleic anhydride react with the zinc oxide, which is a basic material. The alkaline material, which is preferably ammonia but which may be any other alkaline material which volatilizes during the reaction, is in effect displaced by the zinc oxide and does not appear in the final product. Other alkaline materials which may be used include morpholine and 2-amino-l-methyl propiol-l.

In prior processes for using styrene-acrylate copolymers as binders, it has been customary to first form these copolymers and to use these as latices mixed with emulsifiers. The final products in these cases are water-sensitive and hence unsuited for the purposes of the present invention. In my process, however, as already indicated, I copolymerize the styrene-acrylate in the presence of the styrene-maleic anhydride emulsifier, thereby forming a final film which is fully water-insensitive and admirably suited to the making of photoconductive sheets which are useful for making good prints at relative humidities of 75% and above.

The zinc oxide photoconductive material may be used in proportions of 1:1 to 10:1 on the resin and emulsifier solids, by weight. Preferably, about 3 to 5 parts of zinc oxide to one part of said solids, by weight, are used.

The following examples will serve to illustrate this invention in greater detail. Parts are by weight.

**Example I**

100 parts of styrene and ethyl acrylate in the ratio of 35:65 respectively, 20 parts styrene-maleic anhydride, and 3 parts ammonia as 28% ammonium hydroxide are formed into an emulsion by mixing one-half of the styrene-acrylate mixture with the other ingredients mentioned. The emulsion is then kept at 300 parts water and heating to 85-90°C, with stirring and under reflux. As an initiator, 0.5 part benzoyl peroxide may be added. Copolymerization proceeds while the other half of the styrene-acrylate mixture is added dropwise to the reaction vessel. The temperature is maintained, under reflux, until all the aforesaid ingredients have been mixed together, after which heating and stirring continue for about a half hour, by which time complete copolymerization of the styrene-acrylate with the styrene-maleic anhydride has taken place. Any excess monomer is volatilized off by known methods of heat and/or vacuum.

To 100 parts, solids basis of the foregoing mixture are added 400 parts zinc oxide in 400 parts water and 2 parts of a dispersant. The water and dispersant are first mixed, and the zinc oxide is stirred into the mixture. A sodium salt of a carboxy polymer such as "Tamol 731" (sold by Rohm & Haas Chemical Company, Philadelphia, Pa.) is an excellent dispersant for zinc oxide, although other dispersants can be used if they are compatible with the rest of the components of the final coating compositions. Anti-foaming agents may be used if desired; they are preferably volatile (e.g., n-butanol) so that they do not appear in the final product, or if not volatile, they are water-insoluble and do not affect the resistance of the final sheet to high relative humidity.

The addition of the zinc oxide-water-dispersant to the resin solution is carried out slowly enough to avoid coagulation. The resulting coating composition is adjusted to a viscosity (Brookfield viscometer) of 150-400 cps. by addition of water. On the average, about 160 parts water is sufficient for that purpose, but that varies somewhat as the resin emulsions tend to vary in viscosity depending upon their degree of aging.

The resulting composition is coated onto suitable backing, e.g., paper sheets, by appropriate technique such as air knife, wire-wound roll, or reverse-roll coating. The amount of coating thus applied is such as to provide a final dry coating of about 10 to 40 pounds per 3,000 square foot sheet of the paper, and preferably 20 to 30 pounds. The coating is dried and cured at 200-325°C for 3 minutes, during which time the water and any remaining volatiles such as anti-foaming agent and excess monomers are driven off, and polymerization and interaction of the non-volatile components is completed, thereby providing a photoconductive coating consisting of water-insoluble and water-insensitive materials. This coating will consist of approximately 81 parts styrene-acrylate polymer, 16 parts styrene-maleic anhydride complex with the zinc oxide, 40 parts zinc oxide, and 2 parts dispersant. The thus-prepared photoconductive sheet is suitable for making good prints at a wide range of relative humidities, and in particular above 75% R.H.

A number of modifications of the foregoing example are illustrated below. These likewise provide photoconductive sheets suitable for making good prints at a wide range of relative humidities, in particular above 75% R.H. Except as indicated below, the kinds and quantities of ingredients and the conditions of procedure are the same as in Example I.

**Example II**

50 parts styrene, 50 parts ethyl acrylate.

**Example III**

65 parts styrene, 35 parts ethyl acrylate. Heating and stirring continued for 2½ hours instead of 2 hours.

**Example IV**

60 parts styrene, 40 parts butyl acrylate. Heating and stirring continued for 2½ hours instead of 2 hours.

**Example V**

30 parts styrene, 70 parts ethyl acrylate. Heating and stirring continued for 2½ hours instead of 2 hours.

**Example VI**

20 parts styrene, 80 parts methyl acrylate. Instead of the ammonia, 5 parts of morpholine are used to effect solution of the styrene-maleic anhydride.
Example VII

50 parts styrene, 50 parts ethylhexyl acrylate, 15 parts styrene-maleic anhydride, 10 parts 2-amino-1-methyl-propanol-1 (instead of ammonia or morpholine). Heating and stirring continued for 3 hours instead of 2 hours.

Example VIII

5 parts morpholine instead of the ammonia.

Example IX

In accordance with the procedure described in Example I, the following ingredients are mixed as there described and in the proportions shown below:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Styrene</th>
<th>Ethylhexyl acrylate</th>
<th>Styrene-maleic anhydride emulsifier</th>
<th>Oleic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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</table>

In this mixing, 233 parts water are used and 2 parts of ammonia as 28% ammonium hydroxide, to make a 30% solids emulsion. To this emulsion are added 500 parts zinc oxide in 500 parts water and 2½ parts dispersant ("Tamol 731") and the procedure of Example I is followed to provide a coated sheet.

Sheets coated with this composition give satisfactory prints at 80% R.H., though somewhat lighter than those of Examples I–VIII.

Example X

The procedure of any of the foregoing examples can be followed, with satisfactory final photoconductive sheets for the purpose of this invention, by omitting the "Tamol" dispersant entirely. More care is required in mixing, to avoid coagulation and to provide a smooth effective coating composition. When no such dispersant is used, ordinarily no anti-foaming agent is needed.

Modifications of the procedure herein described, within the scope of the appended claims, will be apparent to those skilled in the art.

I claim:

1. Process of making a photoconductive sheet suitable for making prints under a wide range of relative humidity conditions including humidities in excess of 75%, comprising the steps of preparing a water emulsion consisting of a styrene and an acrylate in the ratio of 20 to 70 parts styrene balance alkyl acrylate, a styrene-maleic anhydride copolymer, water, and a volatile alkaline material in an amount sufficient to render said styrene-maleic anhydride copolymer soluble in said emulsion, heating to effect copolymerization of said styrene, acrylate, and styrene-maleic anhydride copolymer, preparing a water dispersion of zinc oxide, uniformly mixing said emulsion and said dispersion with sufficient water to adapt the resulting composition to a coating step, coating said mixture onto a backing sheet, and then heating the resulting coating to drive off water and volatile constituents, and react carboxyl groups of said maleic anhydride with said zinc oxide to form a hydrophobic complex therewith, the final dried product consisting of one to 10 parts zinc oxide to one part of the polymers.

2. Process according to claim 1 wherein about one-half of said styrene and acrylate are initially present in said emulsion, and the balance is added during said first heating step.

3. Process according to claim 1 wherein said styrene, alkyl acrylate, and styrene-maleic anhydride copolymer are in the relative proportions of about 35 parts, 65 parts, and 20 parts, respectively, by weight, and said alkyl acrylate is ethylhexyl acrylate.

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