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3,227,555

RAW STRIPING PROCESS FOR SONOTRACK DISPERSIONS

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No Drawing. Filed Oct. 2, 1961, Ser. No. 141,973
12 Claims. (Cl. 96-84)

This invention relates to sensitized motion picture film having a magnetic sound stripe thereon, and more particularly to a method for adding a sound track to sensitized motion picture film.

It is customary in preparing motion picture film for sound recording to apply to the film a sound track of one of two types, the optical type or the magnetic type. These sound tracks are applied by a variety of ways to the film after the film has been processed. The magnetic method is preferred, since a thin stripe of magnetic oxide in a suitable binder can be coated directly on the processed film and sound recorded thereon.

It has been desired to apply a magnetic stripe to the sensitized motion picture film so that the sound and visual image could be recorded simultaneously. However, there have been many obstacles to preparing such a product. Difficulty has been found in coating the sound track over a sensitized photographic emulsion, and when the sound track was coated on the removable anti-halation backing, it was removed along with backing in the processing solutions.

I have discovered a method of coating a magnetic oxide stripe directly onto the removable anti-halation backing which remains intact through the processing cycle.

One object of this invention is to provide a method for adding a magnetic stripe to sensitized photographic film. An additional object is to provide a method of selectivity insolubilizing an anti-halation coating to prevent its removal in the processing solutions.

The above objects are obtained by applying to the reverse side of sensitized motion picture film an anti-halation layer which comprises a water or alkali-soluble, synthetic colloidal material, such as a cellulose ester or synthetic resin. The cellulose ester is preferably a dicarboxylic acid ester of cellulose, such as cellulose acetate phthalate, cellulose acetate maleate, cellulose acetate succinate, cellulose acetate propionate phthalate, cellulose acetate propionate maleate, or cellulose acetate propionate succinate. The synthetic resin may be a polyvinyl resin such as polyvinyl alcohol esters of dicarboxylic acids having at least 4 carbon atoms, for example polyvinyl phthalate or polyvinyl acetate phthalate or any material whose solubility is derived from carboxyl groups.

Polymeric materials which are operative include those which are polymers used to make film lacquers which can be removed in alkaline processing solutions as described in U.S. application Serial No. 849,465, filed October 29, 1959, in the names of Van Norman and Wagner. However, a tremendous number of compounds can be provided which depend for their solubility on a carboxyl group and which are insolubilized by forming a reaction between this carboxyl group and the diazomethane derivative. Various copolymers and polymers of the acrylic acid derivatives and methacrylic acid derivatives fall into this class of compounds which are operative.

In our preferred embodiment, cellulose acetate phthalate is used which contains colloidal carbon or carbon black, finely dispersed in the coating solution as described in U.S. Patent 2,327,828, issued to Simmons.

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The anti-halation backing is selectively insolubilized by coating the area upon which the magnetic stripe is to be placed with a solution of diazomethane or derivatives thereof, such as diphenyl-diazomethane. Other derivatives which are operative include



in which R_1 and R_2 may be H, C_6H_5 , CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , C_6H_5X in which X may be halogen, methoxy, methyl, or the like. R_1 may be the same as or different from R_2 .

R_1 and R_2 are preferably substituted phenyl groups and may have more than one substituent on each of the phenyl groups without any requirement that the resulting compositions be symmetrical in substituents or that both R_1 and R_2 be substituted phenyl groups. The diphenyl diazomethanes are preferred since they are not as unstable as the simpler compounds which may also be quite poisonous. The substituents on the phenyl groups may be the same as X and may consist of any or all known phenyl substituents with the exception of aldehydes, acidic functions or the p,p',-dimethylamino groups, the latter derivative being extremely unstable and unsoluble.

An alternative method which is our preferred embodiment comprises adding the insolubilizing solvent directly to the magnetic oxide dispersion. An amount of diazomethane or derivative of 0.1% to 5% of the solvent used with the magnetic oxide dispersion is operative in my invention. The solvents with which the diazomethane or derivatives may be mixed are not critical, provided they are compatible organic solvents not containing active hydrogen atoms, e.g. acetic acid. Among the many solvents which may be incorporated into a dispersion of magnetic oxide for use in our invention are the lower aliphatic alcohols, ketones, such as acetone, methyl isobutyl ketone, etc., glycols such as ethylene glycol, etc., Cellosolves, lower alkyl acetates, toluene, benzene, xylene, dioxane, lower ethers, and the like.

The magnetic oxide used can be that normally used for magnetic recording purposes on motion picture films, magnetic tapes, and the like.

The film bases are those well known in the art, such as cellulose triacetate, cellulose acetate butyrate, polyesters, and the like, but other transparent thermoplastic polymers may be used, such as polyolefins, polycarbonates, polystyrene, etc., since the operation of my invention depends upon insolubilizing the anti-halation backing not on the nature of the film base itself.

The following examples are intended to illustrate my invention but not to limit it in any way:

Example 1

Diphenyldiazomethane can be prepared by a method described in "Organic Synthesis," coll. vol. III, p. 351. The material may also be prepared by methods similar to those described in U.S. Patent 2,710,862.

The following discloses a preferred preparation:

In a 250 ml. Erlenmeyer flask were placed 6 g. of benzophenone hydrazone, 100 ml. of hexane, 6.3 g. of silver oxide, and 2 g. of anhydrous magnesium sulfate. The flask was shaken for 1/2 hour at room temperature, a deep red solution resulting. The hexane solution was filtered and placed on an open dish where the hexane was allowed to evaporate, resulting in a very deep red oil which solidified on cooling, M.P. 20-30° C.

A 1.4 g. portion of diphenyl diazomethane was added to 100 g. of magnetic oxide dispersion having the following composition:

	Parts by weight
Iron oxide -----	320
Cellulose nitrate dope -----	640
Butyl Cellosolve -----	200
Ethylene glycol -----	28
Amyl acetate -----	300

The combination was thoroughly mixed and a coating made over a cellulose acetate phthalate anti-halation backing which had been coated on a cellulose triacetate film support. After drying at room temperature, the coating was subjected to a borax sulphate pre-bath for two minutes at room temperature and washed, with rubbing, in a stream of distilled water. The uncoated cellulose acetate phthalate anti-halation backing was completely removed, but the cellulose acetate phthalate under the magnetic oxide coating was untouched, leaving a sound track with clear film support on each said.

Example 2

A sample prepared according to Example 1 was treated with a potassium hydroxide solution (pH 10) for five minutes without disturbing the coating under the magnetic oxide, but which completely removed the remaining anti-halation coating.

Example 3

A sample was prepared according to Example 1 and was immersed in a strongly alkaline Kodak D-8 Developer, containing sodium hydroxide and having a pH of 10. The cellulose acetate phthalate which was uncoated was completely removed from the film base, leaving the magnetic oxide coating untouched.

Although the examples above merely show cellulose acetate phthalate, the mechanism for insolubilizing the coating works equally well with the other alkaline removable anti-halation layers referred to above, and their substitution in the examples results in the same insolubilization of the coating under the magnetic stripe.

The basic or alkaline solutions as defined herein are intended to be those solutions having a pH of 7-14.

My invention may be used for insolubilizing anti-halation layers for marking inks, particularly for use in providing indicating marks for the frame lines on motion picture film which are used for assuring alignment of the films when printing motion picture film. A suitable diazomethane derivative is added to the ink and results in a mark which is not removed in the processing solution.

The processes described herein may also be used for insolubilizing photographic lacquers which are based on the same type of carboxyl containing alkaline soluble material described above.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A process of selectively rendering insoluble to an alkaline solution an area of an alkali soluble layer selected from the class consisting of cellulose and polyvinyl alcohol esters of dicarboxylic acids having at least 4 carbon atoms comprising coating the area to be insolubilized with a solution containing 0.1-5% of a diazomethane derivative.

2. A process of adhering a magnetic stripe to a surface having thereon an alkali soluble layer selected

from the class consisting of cellulose and polyvinyl alcohol esters of dicarboxylic acids having at least 4 carbon atoms comprising coating on the alkali soluble layer a magnetic oxide coating containing 0.1-5% of a diazomethane derivative.

3. A process of selectively rendering insoluble to an alkaline solution an area of an alkali soluble layer selected from the class consisting of cellulose and polyvinyl alcohol esters of dicarboxylic acids having at least 4 carbon atoms comprising coating the area to be insolubilized with a solution containing 0.1-5% of a diazomethane derivative having the following formula:



in which R_1 and R_2 may be H, C_6H_5 , CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , C_6H_5X in which X may be halogen, methoxy, methyl, and R_1 may be the same as or different from R_2 .

4. A sensitized motion picture film having a magnetic stripe coating over an alkali soluble backing layer selected from the class consisting of cellulose and polyvinyl alcohol esters of dicarboxylic acids having at least 4 carbon atoms, the area under the magnetic stripe having been insolubilized by coating with a magnetic oxide coating containing 0.1-5% of a diazomethane derivative.

5. A process of selectively rendering insoluble in alkaline solution an alkali-soluble layer on a photographic film support, comprising applying a solution containing 0.1-5% of a diazomethane derivative to a portion of a layer.

6. A process of selectively rendering insoluble in alkaline solution an antihalation layer on a photographic film support and containing a member of the class consisting of alkali-soluble cellulose esters and synthetic resins, comprising applying a solution containing 0.1-5% of a diazomethane derivative to a portion of the layer.

7. A process of adhering a magnetic stripe to a surface having thereon an alkali soluble layer selected from the class consisting of cellulose and polyvinyl alcohol esters of dicarboxylic acids having at least 4 carbon atoms comprising applying a solution containing 0.1%-5% of a diazomethane derivative to the area to be striped and applying a magnetic stripe to said area.

8. A process of selectively rendering insoluble in alkaline solution an alkali-soluble cellulose dicarboxylic acid ester antihalation layer on a photographic film support, comprising applying a solution containing 0.1-5% diphenyl diazomethane to the layer.

9. A photographic film comprising a support having thereon an alkali-soluble layer an area of which has been rendered insoluble in alkali by applying thereto a solution containing 0.1-5% of a diazomethane derivative.

10. A photographic film comprising a support having thereon an alkali-soluble layer of a member of the class consisting of cellulose and polyvinyl alcohol esters of dicarboxylic acids having at least 4 carbon atoms, an area of said layer having been rendered insoluble in alkali by applying thereto a solution containing 0.1-5% of a diazomethane derivative.

11. A photographic film comprising a support having thereon an alkali-soluble layer of a member of the class consisting of cellulose and polyvinyl alcohol esters of dicarboxylic acids having at least 4 carbon atoms, an area of said layer having been rendered insoluble in alkali by applying thereto a solution contain-

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ing 0.1-5% of a diazomethane derivative having the following formula:



in which R_1 and R_2 may be H, C_6H_5 , CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , C_6H_5X , in which X may be halogen, methoxy, methyl, and R_1 may be the same as or different from R_2 .

12. The element of claim 9 wherein the insolubilized area has been obtained by treatment with diphenyl diazomethane.

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