July 2, 1957 E. M. WEIGEL 2,798,004

FILM LACQUER

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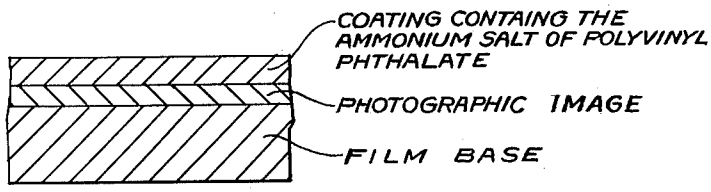
Fig. 1



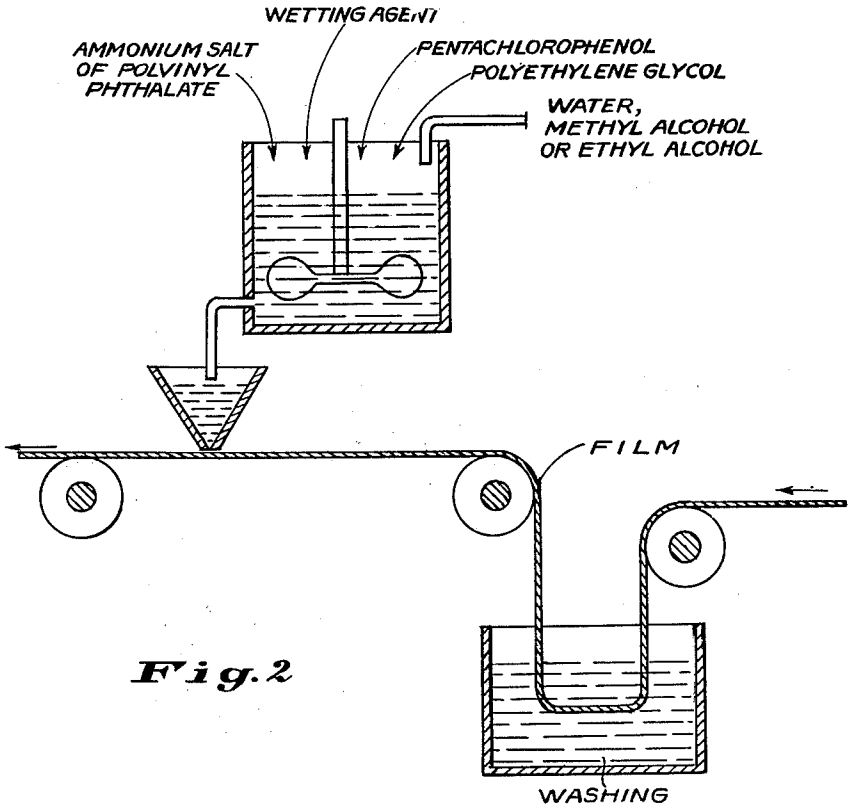


Fig. 2

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FILM LACQUER

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3 Claims. (Cl. 117—2)

This invention concerns a film lacquer for photographic film, more particularly a water-soluble film lacquer comprising the ammonium salt of polyvinyl phthalate and certain compatible constituents which have the property of drying to a water-resistant protective layer.

Due to the nature of photographic film and uses that are made of it, it has been found that handling tends to produce scratches and other abrasions. Moreover the photographic film is subject to fingerprinting, smudging from various lubricating oils, skin oils, etc. These are particularly noticeable in so-called miniature camera film which is passed through automatic printing devices, and in motion picture film which is caused to move through mechanical and manual devices, past foreign surfaces and over other portions of its own surface. A great many lacquers are known which may be applied to photographic films at various stages in their manufacture and use, more particularly following their processing and developing, which may render them protected to some extent against abrasions. However, these lacquers have not met the need for a lacquer that can be applied simply, from non-toxic, non-flammable solvents, at various stages of aqueous film treatments without intermediate drying and handling, which is compatible with photographic emulsions, and which can be removed readily and a fresh coating applied whenever the original lacquer has become excessively damaged. I have discovered that such a film can be produced by using the ammonium salt of polyvinyl phthalate which is water soluble, but which forms a water-insoluble coating on the film. It is removable in the alkaline developing bath commonly used in developing photographic film as well as in other mildly alkaline aqueous solutions.

One object of this invention is to provide a transparent protective layer for photographic elements such as film, paper, glass and the like which may be applied from a water solution. Another object of this invention is to provide a water-insoluble lacquer for photographic elements removable in alkaline developing solutions. A further object of this invention is to provide a transparent protective layer which can resist abrasions, fingerprints, etc. without permitting the photographic image itself to be damaged. Another object is to provide such a protective layer which is readily removable so that when it has become undesirably damaged it can be removed and replaced with a fresh protective layer. Another object is to provide a smooth, transparent layer which can be applied to already scratched and abraded photographic film, in order to minimize the effect of such damage. Another object is to provide a process of applying a protective coating to photographic film which can be economically integrated with the usual operations of photographic film manufacture, processing, and the like. A further object is to provide a water-insoluble coating which can be a vehicle for ultraviolet absorbers. A further object is to provide a transparent protective layer which will have desirable slip and scratch resistance. Another object is to provide a protective layer which

will shield the photographic image from the attack of fungi and other micro-organisms, and which will keep dust, dirt, and contaminants physically separated from the delicate photographic image.

The above objects are carried out by combining polyvinyl phthalate with ammonium hydroxide in distilled water and incorporating in this mixture certain other constituents which will impart additional protective properties to the coating or facilitate the application of defect-free coatings.

To be more specific, I have found that the ammonium salt of polyvinyl phthalate, which is water-soluble, is not stable out of solution, and when dry breaks down to form polyvinyl phthalate which is water-insoluble, and free ammonia. This polyvinyl phthalate is the major film-forming material in my lacquer which also contains materials which insure proper wetting of the film, provide slip and scratch resistance, impart fungicidal properties, and when desirable perform other functions such as absorption and screening of ultraviolet light.

A typical lacquer formula which I have found to carry out the above objects and at the same time to be applicable by dipping and immersion of the film into the solution is as follows:

Polyvinyl phthalate	1.94
Distilled water	96.75
28% ammonium hydroxide	0.96
Carbowax 4000	0.10
Wetting agent	0.24
Pentachlorophenol	0.001
	99.991

Applications of this lacquer may be made to photographic elements which are dry, or in various degrees of wetness so long as the surface water is not so plentiful as to dilute the lacquer excessively; these applications to moist or wet photographic elements are particularly advantageous.

In one embodiment of my invention the lacquer will be applied to photographic elements after processing, between the washing operation that removes final traces of processing chemicals and the drying operation. With miniature camera film or so-called roll films, for example, such processing might be done on a processing machine, with a lacquer-containing tank at the end following the wash tank into which the film would be dipped before transport into the drying section. During manual processing the film would be immersed in a tray of the lacquer after washing and before drying. With motion picture film the photographic processing will usually be done on a continuous machine and the lacquer may be applied after washing. Another embodiment is the application of this lacquer to unexposed and/or unprocessed films for protection of the emulsion surface; such a protective coating would automatically be removed in the developing solutions, permitting normal development of the light-sensitive emulsion. A still further embodiment is the treating of scratched films by reprocessing, through photographic developing and fixing solutions (which has a cleaning action in removing surface dirt and dirt imbedded in scratches), washing, and applicating the lacquer as above in order to minimize the seriousness of the scratches and damage. Photographic elements which have been lacquered may be cleaned by the removal of the lacquer in dilute alkali, facilitating the reapplication of an unblemished lacquer coat. This use of a water-soluble lacquer is especially desirable in simplifying the rejuvenation of dirty and scratched films because more efficient cleaning of the film surface is provided by aqueous cleaning agents, and subsequent lacquer application can be made with a minimum of further treatment.

The polyvinyl phthalate in my lacquer must be chosen so that it meets certain requirements. The phthalyl content must be in such a range as to insure a water-soluble ammonium salt, produced in dilute ammonia solutions and it must have a high enough phthalyl content to avoid the gummy nature of the lower polyvinyl phthalates; usually this will require a phthalyl content between 50–75%.

I have found that the constituents used with the ammonium salt of polyvinyl phthalate may be substituted only with care in order to insure proper compatibility with each other, as well as compatibility with the photographic emulsions upon which they are to be coated.

Carbowax 4000 is the trade name for a solid polyethylene glycol composition made by polymerizing ethylene oxide. It imparts increased scratch resistance and increased slip to the lacquer coating.

A suitable wetting agent which insures the lacquer flowing evenly over the film surface at the time of coating may be a detergent which contains ethylene glycol and an alkyl aryl polyether alcohol. However, this composition may be substituted by certain other detergents, such as Triton 770, Triton X301, Triton X200, Triton X100, glycerol, saponin, Duponol ME or 1,5-naphthalene disulfonic acid (sodium salt). Triton 770 is an aqueous solution 30% sodium salt of an alkyl aryl polyether sulphate and 30% isopropyl alcohol. Triton X301 is the same as Triton 770, but in the form of a 20% aqueous paste without isopropyl alcohol. Triton X200 is similar to Triton X301 except that the active ingredient of the paste is a sulphonate. Triton X100 is an alkyl aryl polyether alcohol. Saponin is composed of a group of amorphous glucosides. Duponol ME is composed of fatty alcohol sulphates.

The amount of ammonia in my lacquer is only so much as to take the polyvinyl phthalate into solution. Methyl or ethyl alcohol may be substituted for water.

The pentachlorophenol is a well known fungicide and preservative, which aids in attaining high resistance to microbiological organism in the final lacquer coatings. Various mercurials, copper naphthenates, and other fungicides and preservatives may be substituted when desired, so long as they are compatible.

Polyvinyl phthalate renders a coating superior to some other compounds in that it is unaffected by carbon tetrachloride, a common film cleaning material which dissolves many other film lacquers. Also polyvinyl phthalate in the ammonium salt is applied from water, not from toxic and/or inflammable solvents, and being water-soluble, it may be applied immediately following the last wash on a processing machine when the lacquer is applied as a protective coating for the developed film. No specialized equipment is required (such as a lacquering machine); therefore, extra operations with extra handling are eliminated.

The insolubilization of the lacquer is a time-temperature relationship and proceeds more rapidly as the temperature is increased. The bulk of the ammonia is lost readily as the water first evaporates from the lacquer, and then retained ammonia is lost more slowly over a period of several hours to several days, depending upon conditions such as temperature, air flow, etc. However, it appears that normal motion picture film drying is sufficient to remove most of the combined ammonia, and this drying plus the normal interval between processing and use renders the lacquer insoluble in water and secures its final desirable physical qualities.

In the accompanying diagrammatic illustration, Fig. 1 shows a film base carrying a photographic image and superimposed thereon a coating containing the ammonium salt of polyvinyl phthalate. It will be understood, of course, that when this coating dries, the ammonia evaporates leaving water insoluble polyvinyl phthalate.

Fig. 2 is a flow diagram showing that the ammonium salt of polyvinyl phthalate, a wetting agent, pentachlorophenol, water-soluble polyethylene glycol and water (or similar material) are admixed to form the coating composition which is then coated on the processed photographic film using a suitable coating technique such as the hopper method illustrated.

Although our preferred embodiment comprises coating the ammonium salt out of water, polyvinyl phthalate may be coated out of organic solvents, such as cellosolve, lower aliphatic alcohols such as methyl, ethyl, isopropyl, isobutyl and the like, aromatic hydrocarbons such as benzene toluene, xylene or mixtures of organic solvents which are compatible.

The properties of the hardened lacquer appear to be comparable whether coated out of organic solvents or out of water. Tests run on samples of photographic film indicate that the treated films are considerably superior to untreated film in their resistance to abrasive action. For instance, strips were run through a rapid type printer and compared with uncoated check strips which showed greater damage as a result of the printing operation. In further tests, larger samples of photographic films were subjected to a modified ASTM Falling Carborundum Test. Haze measurements indicate quite definitely that the lacquered materials were more resistant to abrasion than untreated controls. The treated film is found resistant to fingerprinting; usually the fingerprint is removable by wiping with a dry cloth or a cloth moistened with carbon tetrachloride or other film cleaning solvent; in severe cases the lacquer can be removed by reprocessing the film through normal alkaline developer, or rinsing in dilute alkali of pH between 8.0 and 12.0, followed by a water rinse, and reapplication of the lacquer—this renewal is almost invariably sufficient to eliminate the most stubborn fingerprints. Tests of microbiological resistance wherein treated film is exposed to conditions of high humidity etc. favoring the growth of micro-organisms in both accelerated tests and in tropic regions, have shown the treated film to resist solubilization of the photographic emulsion and obliteration or destruction of the photographic image under conditions in which untreated films are rendered useless in relatively short times.

Ultraviolet absorbers which may be used depend upon their compatibility and solubility in the desired solvents. Such compounds include 2,2′-dihydroxy-4,4′-dimethoxybenzophenone, 2,2′-dihydroxy-benzophenone, sodium-(α-phenylhydrazone)-α,β-diketobutyrate, Thioflavine S, derivatives of α-methyl-α-phenyl hydrazine, and the like.

What I claim is:

1. A photographic product comprising a support member carrying a photographic image produced by exposing and processing a light-sensitive photographic emulsion and superimposed upon the photographic image, a protective coating of polyvinyl phthalate produced from a coating composition containing 1.0 to 10.0% polyvinyl phthalate having a phthalyl content between 50–75% dissolved in an amount of ammonium hydroxide sufficient to form a stoichiometric equivalent to the polyvinyl phthalate, about 0.24% of a wetting agent selected from the group consisting of saponin, fatty alcohol sulphates, alkyl aryl polyether alcohol, and the sodium salt of 1,5-naphthalene disulfonic acid, and from .05 to .5% solid water-soluble polyethylene glycol.

2. A process for protecting processed photographic film from scratches and similar abrasions comprising coating the processed film with a water-soluble coating composition comprising from about 1.0 to 10.0% polyvinyl phthalate having a phthalyl content between 50–75% in an amount of ammonium hydroxide sufficient to form a stoichiometric equivalent to the polyvinyl phthalate, about 0.24% of a wetting agent selected from the group consisting of saponin, fatty alcohol sulphates, aryl polyether sulphate, alkyl aryl polyether alcohol, and the sodium salt of 1,5-naphthalene disulfonic acid, and from .05 to .5% solid water-soluble polyethylene glycol.

3. A process for rejuvenating soiled processed photo-

graphic film comprising coating said film with a coating composition comprising polyvinyl phthalate having a phthalyl content between 50–75% in an amount of ammonium hydroxide sufficient to form a stoichiometric equivalent to the polyvinyl phthalate, about 0.24% of a wetting agent selected from the group consisting of saponin, fatty alcohol sulphates, aryl polyether sulphate, alkyl aryl polyether alcohol, and the sodium salt of 1,5-naphthalene disulfonic acid, and from .05 to .5% solid water-soluble polyethylene glycol, reprocessing, washing and recoating said film with the said coating.

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