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(54) Photographic assembly.

(57) The present invention provides a photographic film assembly which comprises coated on a sub-coated cellulose triacetate or cellulose acetate-butyrate base at least one gelatino silver halide emulsion layer wherein the silver halide emulsion layer which is closest to the base comprises from 1 to 30% by weight of the gelatin in the emulsion layer, a latex polymer whose glass transition temperature does not exceed 30 °C and which to a copolymer of an ethylenically unsaturated monomer containing an aromatic moiety, with an acrylate ester monomer. The latex polymer may also contain additional ethylenically unsaturated monomers. Preferably the amount of latex present in the silver halide emulsion layer is from 2 to 10% by weight of the gelatin in the layer.

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This invention relates to photographic silver halide emulsion assemblies.

Most camera films consist of a photographic assembly which comprises at least one silver halide emulsion layer coated on a cellulose triacetate or cellulose acetate-butyrate base. Gelatin layers can be coated on to such base materials without the need to treat the base to the same extent as that which is required to render polyethylene terephthalate (polyester) bases capable of being coated with a gelatin layer. Nevertheless all cellulose triacetate or cellulose acetate-butyrate base is supplied to the manufacturers of photographic materials treated in some way to help a gelatin coat to adhere thereto better than untreated base. Each base manufacturer has his own method of treating cellulose-derived bases and often the photographic manufacturer is not privy to the method employed by the base manufacturer. It is thought that some base manufacturers apply a coating of partially hydrolysed cellulose mixed with gelatin to the surface of the cellulose triacetate or cellulose acetate-butyrate. Sometimes this first coating is coated with a thin gelatin layer. Such cellulose triacetate or cellulose acetate-butyrate base which has been treated by the base manufacturer to render it more susceptible to be coated with a gelatin layer is hereinafter referred to as sub-coated cellulose triacetate or cellulose acetate-butyrate base.

Unfortunately due to the increasingly vigorous processing conditions now being used to process camera films such as roller processors using fairly high temperature processing solutions, constant agitation of the processing solutions and high temperature drying conditions, camera films coated on sub-coated cellulose triacetate or cellulose acetate-butyrate are apt to exhibit poor adhesion of the emulsion layers to the base.

It is the object of the present invention to provide a photographic film assembly wherein the base is sub-coated cellulose triacetate or acetate butyrate which exhibits markedly improved adhesion of the emulsion layers to the base even when subjected to vigorous processing conditions.

Therefore according to the present invention there is provided a photographic film assembly which comprises coated on a sub-coated cellulose triacetate or cellulose acetate-butyrate base at least one gelatino silver halide emulsion layer wherein the silver halide emulsion layer which is closest to the base comprises from 1 to 30% by weight of the gelatin in the emulsion layer, a latex polymer whose glass transition temperature does not exceed 30°C and which is a copolymer of an ethylenically unsaturated monomer containing an aromatic moeity, with an acrylate or methacrylate ester monomer. The latex polymer may also contain additional ethylenically unsaturated monomers, as described below.

Preferably the amount of latex present in the silver halide emulsion layer is from 2 to 10% by weight of the gelatin in the layer.

Examples of the monomers which are useful to prepare the latex used in the present invention are:-

As monomers containing an aromatic moeity:-

styrene, vinyl toluene, 2,4-dimethylstyrene, -methyl styrene, divinyl benzene, vinylnaphthalene, 4-methoxystyrene, 3-nitrostyrene, vinyl phenol, vinyl benzoate, diallyl phthalate, benzyl methacrylate, phenyl methacrylate, N-phenylacrylamide, 2-phenylethylmethacrylate. As acrylate or methacrylate monomers Cyclohexyl methacrylate, 2-hydroxy-propylmethacrylate, 2-hydroxyethylmethacrylate, ethylene glycol dimethacrylate, butyl acrylate, methyl acrylate, ethyl acrylate, 2-ethylhexylacrylate, methyl methacrylate, n-heptyl acrylate. As comonomers which may be present vinyl cyclohexane, acrylonitrile, vinylidene chloride, vinyl acetate, vinyl propionate, vinyl stearate, acrylic acid and its salts, 2-acrylamido-2-methyl propane sulphonic acid and its salts, acrylamide, methacrylamide, N-vinyl pyrrolidone, ethylene sulphonic acid and its salts.

Preferred combinations of monomers are styrene/butyl acrylate; vinyl toluene/butyl acrylate; styrene/ethylhexyl acrylate; styrene/ethyl acrylate; styrene/n-heptyl acrylate; -methyl styrene/butyl acrylate; styrene/divinyl benzene/butyl acrylate; styrene/methyl methacrylate/ butyl acrylate; styrene/2-hydoxypropylmethacrylate/butyl acrylate; styrene/butyl acrylate/2-acrylamido-2-methylpropane sulphonic acid sodium salt.

These combinations may include monomers in varying proportions but they preferably contain at least about 10% by weight of the aromatic ethylenically unsaturated monomer. Preferably they contain at least 20% by weight of the acrylate or methacrylate ester monomers.

Particularly preferred combinations are styrene 50 parts, butyl acrylate 50 parts; vinyl toluene 50 parts, butyl acrylate 50 parts; and styrene 50 parts, ethyl hexyl acrylate 50 parts. The parts being by weight.

The preparation of latices of the above type requires the use of one or more surface active agents, and these may be any of the types well known in the art. In particular, anionic surfactants are very useful and these may be used optionally in the presence of a nonionic surfactant.

The anionic surfactants may be the sodium, potassium or ammonium salts (but preferably the sodium salt) of a sulphate, sulphonate, phosphonate or phosphate derivative. The hydrophobic part of the surfactant may be an alkyl group, an aryl group, or a combination of an alkyl and an aryl group. The hydrophilic part of the surfactant may contain, in addition to an anionic group, an alkylene oxide chain with up to 50 alkylene oxide units in the chain. In addition, there may be present ethylenically unsaturated units in the surfactant thus enabling it to copolymerise with the other units and thus render the surfactant substantive. The non-ionic surfactants may contain alkyl, aryl or alkyl-aryl groups together with alkylene oxide chains; there are many other suitable nonionic surfactants well known in the art, and these include: alkylolamides; carbohydrate derivatives such as glucosides; alkylesters; and amine oxides. A large number of surfactants are commercially available and details of many suitable types may be found for example in "Surfactants UK", ed. G.L. Hollis, published by Tergo-Data, England. The surfactants may comprise from 0.1 to 15% by weight of the total latex.

Preferred surfactants to use to prepare the latexes used in the present invention are alkyl phenol ethoxylate sulphates, alkyl sulphonates, sulphosuccinate esters and aryl-and alkyl ethoxylate phosphates, in combination with or in the absence of alkyl phenol ethoxylates, alkylphenol polyglycidolethers or alkanol ethoxylates.

Initiators suitable for the preparation of the latexes used in the present invention may be selected from those well known in the prior art. These are usually water soluble azo compounds or water soluble per-oxo compounds. For example, the sodium salt of azobis (cyanopentanoic acid) is a commonly available water soluble azo initiator. Sodium and potassium persulphate are very commonly used in emulsion polymerisation. Hydrogen peroxide and some other peroxides such as tertiary butyl hydroperoxide are also useful initiators. The initiation process may be effected either at higher temperatures (e.g. above about 70 ° C) by using an initiator which decomposes thermally or at lower temperatures (e.g. below about 70 ° C) by initiator couples which act by a redox system. Details of these initiation processes may be found for example in "Emulsion Polymerisation" by D.C. Blackley, Applied Science Publishers, London, 1975. The initiators may comprise from 0.1 to 1.0% by weight of the reaction mixture.

The procedure for preparing the latexes used in the present invention follows that commonly used in emulsion polymerisation. Typically, the mixture of monomers is added, over a period of from thirty minutes to three hours, to a heated, oxygen-free solution of the chosen surfactant in water and the selected initiators and further surfactant are added either continuously or portionwise over the same period. Following the polymerisation it is necessary to cool the reaction mixture to ambient temperature followed by filtration to remove small quantities of coagulated polymer.

In the preparation of the latex there may be small quantities of a variety of additives including biocides and colloid stabilisers. During the polymerisation it may be desirable to limit the molecular weight of the polymer by adding small amounts of chain transfer agents. Additives such as this are covered in Blackley's book (see above).

Procedure

A mixture of 934g of butyl acrylate and 944g of styrene was added at a constant rate over a period of 3 hours to a stirred, aqueous solution consisting of water (1739g), potassium persulphate (4.65g), sodium metabisulphite (2.05g), and the sodium salt of a nonylphenol ethoxylate sulphate surfactant (167g of a 25% active solution), maintained at 70 ° C. Simultaneously with the monomer solution, a further solution of the same surfactant (500g of a 25% solution), potassium persulphate (2.32g) and sodium metabisulphite (1.02g) in 650g water was added.

The mixture was maintained at 70 ° C for 4 hours before cooling to below 30 ° C and filtering through a 100um sieve.

There was obtained a latex having a solids content of 40%, particle size 114nm. The Tg of the polymer is +3 ° C. This is latex 1.

Latices 2 - 6

Using a similar method to that described in the above procedure, the following latices were prepared as shown in Table 1.

Table 1

Latex	Monomer Composition	Surfactant	Surfactant: Monomer ratio
2	Butyl acrylate (24%), 2-Hydroxypropyl-methacrylate (76%)	Nonyl phenol ethoxylate phosphate (83%), Nonyl phenol ethoxylate (17%)	1:24
3	Butyl acrylate (45%), Methyl methacrylate (55%)	As in the Procedure	1:4.3
4	Butyl acrylate (53%), Methyl methacrylate (25%), 2-Hydroxy-propyl methacrylate (22%)	Nonyl phenol ethoxylate phosphate (67%), Nonyl phenol ethoxylate (33%)	1:22.6
5	Vinyl toluene (50%), Butyl acrylate (50%)	As in the Procedure	1:15
6	Styrene (50%), Ethylhexyl acrylate (50%)	As in the Procedure	1:15

The silver halide present in the emulsions used in the assembly of the present invention may be of any silver halide composition, eg. pure silver bromide, silver iodobromide, silver chloroiodobromide, silver chloride, silver chlorobromide. The silver halide grains in the emulsion may be of any habit eg, tabular or cubic. They may have been chemically sensitised for example by gold and/or sulphur. They may have been optically sensitised by use of any of the well known merocyanine or methin cyanine dyes used for this purpose. The emulsion may contain any of the well known stabilisers, hardening agent and any of the other well known additives often present in camera film silver halide emulsions.

There may be at least two silver halide emulsion layers and the top-most silver halide emulsion layer may be coated with a gelatin supercoat or non-stress layer which may comprise antiblocking agents. There may be gelatin based inter-layers between any of the silver halide emulsion layers.

There may be on the reverse side of the cellulose triacetate or cellulose acetate butyrate base to that side which carries the emulsion layer or layers at least one backing layer which may be an anti-halation backing layer.

The accompanying examples will serve to illustrate the invention.

EXAMPLE 1

Strips of a photographic material were prepared from a typical assembly made from a sub-coated base of cellulose triacetate film to prepare a high sensitivity black and white negative photographic material. The total silver content of the film was 8.0 - 7.0 g/m^2.

COMPOSITION OF PHOTOGRAPHIC LAYERS

The amount of coating is expressed for each of the layers in terms of g/m^2; the amount of silver halide expressed in terms of the weight of silver.

Layer 1. First Emulsion Layer

Silveriodobromide particles	1.5 g/m^2
(AgI = 7.4 mol % I)	
1.165 um average particle size	
Silveriodobromide particles	1.5
(AgI - 6.0 mol% I)	
0.752 um average particle size	
Gelatin	3.87
Latex 1	0.2

Layer 2. Second Emulsion Layer coated on layer 1

Silveriodobromide particles	3.5
(AgI = 7.4 mol % I)	
1.165um average particle size	
gelatin	5.14

Layer 3 Protective Layer	
Gelatin	1.2
Polystyrene particles (as antiblock) (2.8um diameter)	0.012
anionic fluorinated wetting agent	0.20

In this Example, 0.2g/m^2 of latex corresponds to 5% of the weight of the gelatin present in the first emulsion layer.

Examples 2 - 6

Similar strips of photographic assemblies were prepared using a similar formulation to that described in Example 1, but wherein the following latices were used:-

Example	2	Latex	2	Tg	-24°C
"	3	"	3	"	+10°C
"	4	"	4	"	- 5°C
"	5	"	5	"	+3°C
"	6	"	6	"	+3°C

As set forth in TABLE 1

TABLE 2

Effect of latex addition on wet adhesion after processing.				
Latex (0.4g/m^2)	Adhesion Grade after/days			
	7	14	21	29
1	1	1	1	1
2	4	4	5	4
3	2	2	5	2
4	5	4	3	4
5	1	2	1	1
6	1	1	1	1
# Control	5	5	5	5

Control no Latex

TABLE 3

Effect of Latex Quantity on Wet Adhesion after processing					
Latex 1 g/m^2		Adhesion Grade after/days			
		8	14	21	30
	0	5	2	4	5
1%	0.05	5	1	2	3
2%	0.1	1	1	1	1
5%	0.2	1	1	1	1
10%	0.4	1	1	1	1
The percentages are the percent of latex of the gelatin in the emulsion.					

ADHESION MEASUREMENT

In the wet adhesion test, the film is scratched at various stages of the processing cycle and then rubbed with the finger.

Adhesion grade is assigned according to the amount of emulsion removed when the film is rubbed. The grades are described as follows:

Grade 1 - No adhesion failure observed
Grade 2 - Minor frilling of emulsion at scratch edge
Grade 3 - Minor stripping of emulsion at scratch edge
Grade 4 - Obvious stripping of emulsion
Grade 5 - Severe stripping of emulsion

The wet adhesion test is carried out 7 days after coating.

Strips of the photographic material prepared in Examples 1, 5 and 6 together with a control strip which comprised no latex were exposed to a step wedge and the sensitometric properties were compared with the control. The photographic foot speed S0.1 of all the strips was substantially the same as was the contrast G. This showed that the presence of the latex in the emulsion had no deleterious effect on the sensitometric properties of the assembly.

For the wet adhesion tests the photographic assemblies were processed in a developer at 25°C. They were then fixed in an ammonium thiosulphate fixing bath and the water washed.

All this processing took place in an automatic roller processing machine in which there was constant agitation of the processing solutions and the wash water.

The developer used had the following formula:-

Metol	2.0g
Hydroquinone	5.0g
Sodium sulphite	100.0g
Borax	2.0g
Water to	1 litre

From these results it can be seen that the latexes which comprise an aromatic moiety provide good adhesion, that is to say latexes 1, 5 and 6. However, latexes which comprise no aromatic moiety had inferior or bad adhesion that is to say latexes 2, 3 and 4.

Claims

1. A photographic film assembly which comprises coated on a sub-coated cellulose triacetate or cellulose acetate-butyrate base at least one gelatino silver halide emulsion layer characterised in that the silver halide emulsion layer which is closest to the base comprises a latex polymer whose glass transition temperature does not exceed 30°C and which is a copolymer of an ethylenically unsaturated monomer containing an aromatic moeity, with an acrylate or methacrylate ester monomer, the latex comprising from 1 to 30% by weight of the gelatin in the emulsion layer.

2. A photographic film assembly according to claim 1 characterised in that the amount of latex present in the silver halide emulsion layer is from 2 to 10% by weight of the gelatin in the layer.

3. A photographic film assembly according to either claim 1 or claim 2 characterised in that the latex is derived from one of the following combinations of monomers:- styrene/butyl acrylate; vinyl toluene/butyl acrylate; styrene/ethylhexyl acrylate; styrene/ethyl acrylate; styrene/n-heptyl acrylate; -methyl styrene/butyl acrylate; styrene/divinyl benzene/butyl acrylate; styrene/methyl methacrylate/butyl acrylate; styrene/2-hydoxypropylmethacrylate/butyl acrylate; styrene/butyl acrylate/2-acrylamido-2-methylpropane sulphonic acid sodium salt.

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EUROPEAN SEARCH REPORT

Application Number
EP 93 10 1989

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 197 127 (THOMAS G. MECCA) * column 5, line 6 - line 9 * * column 6, line 15 - column 7, line 3; claims 1-24 * ---	1-3	G03C1/053
A	FR-A-2 208 136 (ILFORD LIMITED) * claims 1-9 * ---	1-3	
A	EP-A-0 358 187 (EASTMAN KODAK COMPANY) * page 8, line 5 - page 9, line 11; claims 1-5 * * examples * -----	1-3	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 MAY 1993	HINDIAS E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document