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PHOTOGRAPHIC MATERIALS

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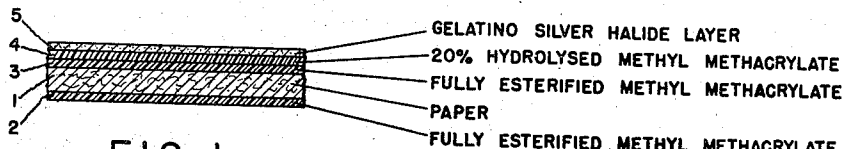


FIG. 1

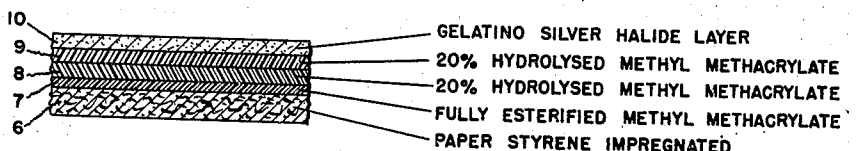


FIG. 2

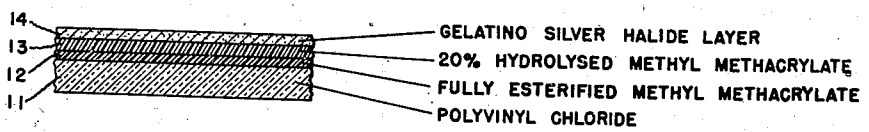


FIG. 3

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PHOTOGRAPHIC MATERIALS

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7 Claims. (Cl. 95—9)

This invention relates to photographic materials and particularly to photographic elements comprising a gelatino layer, e. g. a gelatino silver halide emulsion layer, carried on a hydrophobic support.

Photographic elements generally speaking comprise a gelatino silver halide emulsion coated on a supporting sheet of paper, glass or cellulose derivative film. In recent years there have been developed a large number of synthetic colloid materials which can be used as supports for the silver halide emulsion. By selection from among such materials supports can be made which have physical characteristics rendering them suitable for special purposes. For example, a sheet of methyl methacrylate polymer may be used as a substitute for glass with the advantages of reduced weight and brittleness; sheets of polystyrene may be used where a support of high water resistance is required; and flexible supports resembling rubber may be prepared from plasticized polyvinyl chloride. Synthetic colloid materials are also of use in modifying the properties of the more conventional supports. For example a fibrous cellulosic support such as paper, or a colloid film support such as a cellulose or cellulose nitrate or cellulose acetate film, may be made more resistant to water by providing it with surface coatings of a composition containing a highly hydrophobic synthetic colloid such as polystyrene or methyl methacrylate polymer, compare, for example, British Patent No. 513,238.

However, when a gelatino photographic emulsion is coated directly on a hydrophobic colloid surface, the degree of adhesion effected is frequently insufficient for photographic purposes and it is therefore the practice, for example when coating a gelatino silver halide emulsion on cellulose nitrate or cellulose acetate film base, to provide a layer (known as a substratum) between the support and the emulsion to secure good anchorage between the layers.

With supporting surfaces of synthetic hydrophobic colloids such as alkyl methacrylate polymer there is some difficulty in securing adequate adhesion, and the types of substratum commonly used in securing adhesion of gelatino silver halide emulsions to cellulose acetate and cellulose nitrate supports are not very suitable.

Alkyl methacrylate polymers vary in constitution according to the degree of esterification of the methacrylic acid residues, and it has now been discovered that gelatino photographic emulsions can be satisfactorily anchored to highly esterified alkyl methacrylate polymers by providing a substratum of an alkyl methacrylate polymer of lower degree of esterification, i. e. containing more free carboxyl groups.

According to the present invention, therefore, photographic elements are provided which comprise a support having a surface of a highly esterified (including fully esterified) alkyl methacrylate polymer, one or more substrata containing alkyl methacrylate polymer of lesser degree of esterification coated on said surface, and a gelatino layer, e. g. a photographic gelatino emulsion layer, coated on such substratum or on the outermost of such substrata.

More particularly the invention is concerned with the case where the alkyl methacrylate polymer is a methyl methacrylate polymer.

Methyl methacrylate polymer as commercially available, e. g. as the product sold under the registered trade mark "Diakon," is substantially fully esterified, i. e. it contains no free carboxyl groups. Methyl methacrylate polymers containing some free carboxyl groups may be prepared by the co-polymerisation of methyl methacrylate and methacrylic acid in solution in a common solvent, for example methyl alcohol and benzene, by heating the solution in the presence of a polymerisation catalyst such as benzoyl peroxide. Another method, somewhat simpler, is to effect the partial hydrolysis of a fully esterified methyl methacrylate polymer by means of acid or alkali. In general acid hydrolysis in solution is preferred, and particularly hydrolysis by means of sulphuric acid.

Methyl methacrylate polymer, for example that sold under the registered trade-mark "Diakon," may be dissolved in cold aqueous sulphuric acid containing up to 35% by volume of water. The polymer may then be hydrolysed by heating the solution. The degree of hydrolysis may be controlled by regulating the proportion of sulphuric acid to water in the solution and the temperature and duration of the heating. While concentrated sulphuric acid may be used for dissolving the polymer, the process is then somewhat more difficult to control as the acid is liable to cause breakdown of the polymer structure, resulting in dark-coloured products of impaired film-forming capacity. Generally speaking a given degree of hydrolysis may be achieved by employing a high temperature and a short time of heating, or a lower temperature and a longer time. The temperature and time are preferably chosen so as to allow of accurate reproducibility from one batch to another. The fol-

lowing table indicates typical results obtained by sulphuric acid hydrolysis, the degree of hydrolysis being expressed on the basis that 100% hydrolysis represents complete conversion of the methyl methacrylate polymer to polymethacrylic acid.

Acid mixture		Temperature of reaction	Time of reaction	Per cent hydrolysis
Sulphuric acid	Water			
Cc.	Cc.	° C.		
70	30	60	20 mins.	2.7
70	30	60	115 mins.	4.7
70	30	70	60 mins.	15.3
70	30	70	150 mins.	30.9
100	Nil	20–25	4 days.	67.5

When the hydrolysis has reached the desired stage the polymer may be precipitated by pouring the solution into water, and the precipitate washed first with water and then with ethyl alcohol. The polymer may then be purified by redissolving it in acetone and reprecipitating with water and may then be pressed free of entrained water and dried, for example at 100° C.

With increasing degrees of hydrolysis, i. e., with increasing content of free carboxyl groups, the solubility of the resin in common solvents varies progressively. Thus, whereas "Diakon F" is soluble in acetone, the partially hydrolysed products are increasingly less soluble in acetone as the degree of hydrolysis increases, so that, for example, a product hydrolysed to the extent of about 66% is insoluble in pure acetone, though soluble in acetone containing 20% water, and a product hydrolysed to the extent of about 77% is insoluble in pure acetone, though soluble in acetone containing 50% water. The products are insoluble in water alone, though the more highly hydrolysed products swell in water. The less hydrolysed products are insoluble in aqueous ammonia, but with increasing degree of hydrolysis beyond about 15% become soluble in aqueous ammonia.

The optimum degree of hydrolysis of the methyl methacrylate polymer to be used in the substratum must, of course, be selected with regard to the degree of esterification of the methyl methacrylate polymer surface on which it is to be coated and with regard to the character of the gelatino emulsion layer which is to be coated on it. If the degree of hydrolysis is too little adhesion of the gelatino emulsion will not be wholly satisfactory, whilst if the degree of hydrolysis is too great so that there is too wide a difference between the degree of esterification of the supporting surface and of the substratum adhesion between these two will not be wholly satisfactory. In general, with a supporting surface consisting of substantially fully esterified methyl methacrylate polymer and a normal gelatino silver halide emulsion, a substratum containing a methyl methacrylate polymer hydrolysed to the extent of 15 to 25% is satisfactory.

In the photographic elements of this invention the support may be wholly composed of methyl methacrylate polymer, or supports primarily composed of other materials but having a surface coating of methyl methacrylate polymer may be employed, for example the materials described in British Patent No. 513,238. Thus, for example, the support may consist of paper, or cellulose or cellulose derivative, or hydrophobic colloids such as plasticised polyvinyl chloride or polystyrene, coated with a layer of methyl methacrylate polymer. Other layers may be present in the support as desired providing that the surface layer is a methyl methacrylate polymer. For example, a support having a basis of cellulose acetate may have a surface layer of cellulose nitrate, or a support having a basis of polyethylene may have a surface layer of polystyrene, and such surface layer may be coated with methyl methacrylate polymer.

Whilst the substratum may contain the methyl methacrylate polymer containing free carboxyl groups as the sole film-forming ingredient, it is generally preferred to include in it a proportion of gelatin. If desired several substrata may be applied in succession, e. g. first a substratum containing methyl methacrylate polymer containing free COOH group as the sole film-forming ingredient, and then a substratum containing both the methyl methacrylate polymer containing free COOH group and gelatin. If desired, this latter layer may be followed by, or substituted by, a substratum in which the sole film-forming colloid is gelatin; in this case the gelatin substratum coating solution should preferably contain a proportion of organic solvent for the methyl methacrylate polymer in the underlying substratum. A gelatino photographic emulsion layer may then be coated on the gelatin substratum.

It will be appreciated that the methyl methacrylate polymers employed according to this invention should not be soluble in any processing solution, e. g. photographic developer, with which the final product may be treated.

The following examples illustrate the invention:

Example I

A photographic support 1 as shown in Figure 1 of the drawing of paper was rendered more resistant to water by coating its surfaces with the following solution:

Fully esterified methyl methacrylate polymer (Diakon "D")	gm.	10
Toluene	cc.	75
Ethyl alcohol	cc.	15

These coatings 2 and 3 were dried and the following solution applied to form a substratum:

Gelatin	gm.	5
Distilled water	cc.	25
Salicylic acid	gm.	2.5
Methyl alcohol	cc.	175
Acetone	cc.	800
40% Formaldehyde	cc.	0.5
Methyl methacrylate polymer hydrolysed to the extent of 20%	gm.	5

When the substratum 4 was dry a coating 5 of gelatino silver halide emulsion was applied. Excellent adhesion was obtained between all the layers.

Example II

A paper support 6 as shown in Figure 2 of the drawing was rendered translucent by passing it through the following solution, which was maintained at a temperature of about 120° C:

Polystyrene	gm.	30
Tri-cresyl phosphate	cc.	5
Xylene	cc.	65

The impregnated paper was dried and was then coated with the following solution:

Fully esterified methyl methacrylate polymer (Diakon "D")	gm.	20
Methyl ethyl ketone	cc.	500
Amyl acetate	cc.	500

The surface of the methyl methacrylate polymer layer 7 was then coated with the following solution to form a first substratum 8:

Methyl methacrylate polymer hydrolysed to the extent of 20%	gm.	10
Methyl ethyl ketone	cc.	1000

The surface of this substratum was then coated with the following solution to form a second substratum 9:

Gelatin	gm.	5
Distilled water	cc.	25
Salicylic acid	gm.	2.5
Methyl alcohol	cc.	175
Acetone	cc.	800
40% Formaldehyde	cc.	0.5
Methyl methacrylate polymer hydrolysed to the extent of 20%	gm.	2

A coating 10 of gelatino silver halide emulsion was then applied to the surface obtained. Excellent adhesion between all the layers was thus effected.

Example III

A support 11 as shown in Figure 3 of the drawing of plasticised polyvinyl chloride was coated with a 2% solution of a fully esterified methyl methacrylate polymer in methyl ethyl ketone and the surface of the coating 12 was then coated with the following solution to form a substratum 13:

Gelatin	gm.	5
Salicylic acid	gm.	2.5
Distilled water	cc.	25
Methyl alcohol	cc.	125
Acetone	cc.	850
40% Formaldehyde	cc.	0.5
Methyl methacrylate polymer hydrolysed to the extent of 20%	gm.	4

After drying, the substratum was coated with a gelatino silver halide emulsion to form layer 14. Excellent adhesion between the layers was obtained.

Whilst the invention has been described with particular reference to the coating of gelatino silver halide emulsion layers on the supports, it will be appreciated that other gelatino photographic layers may be coated on the supports with the assistance of the substrata of this invention, e. g. bichromated gelatin layers, as may also any plain, dyed or pigmented gelatin layers.

While the invention has been described with particular reference to the coating of a gelatino emulsion layer on a support, it will be appreciated that the procedure may be inverted. Thus a gelatino emulsion layer coated on a support may be supercoated first with a methyl methacrylate polymer of low degree of esterification and then with a methyl methacrylate polymer of higher degree of esterification. This form of the invention has some value where it is desired to protect an already formed photographic image, as in kine film. It will be appreciated that this form of the invention is fundamentally the same as the form of the invention described in greater detail above since the final product includes, as the fundamental assembly, a layer of alkyl methacrylate polymer, a layer of alkyl methacrylate polymer of lower degree of esterification, and a gelatin emulsion layer.

What we claim is:

1. A photographic element which comprises a support having a surface of a substantially fully esterified methyl methacrylate polymer, at least one substratum layer adjacent thereto and having a methyl methacrylate polymer containing 15 to 25% free carboxyl groups, and a gelatino layer adjacent to said substratum layer.

2. A photographic element which comprises a support having a surface of a substantially fully esterified methyl methacrylate polymer, a substratum layer adjacent thereto containing gelatin and a methyl methacrylate polymer having 15 to 25% free carboxyl groups, and a gelatino layer adjacent to said substratum layer.

3. A photographic element which comprises a support having a surface of a substantially fully esterified methyl methacrylate polymer, a first substratum layer adjacent thereto containing a methyl methacrylate polymer having 15 to 25% free carboxyl groups, a second substratum layer adjacent to the first containing gelatin and a methyl methacrylate polymer having 15 to 77% free carboxyl groups, and a gelatino layer adjacent to said second substratum layer.

4. A photographic element which comprises a support having a surface of a substantially fully esterified methyl methacrylate polymer, a first substratum layer adjacent thereto containing a methyl methacrylate polymer having 15 to 25% free carboxyl groups, a second substratum layer adjacent to the first containing gelatin and a methyl methacrylate polymer having 15 to 77% free carboxyl groups, a third substratum layer consisting essentially of gelatin, and a gelatino silver halide emulsion layer adjacent to said third substratum layer.

5. A photographic element which comprises a support having a surface of a substantially fully esterified methyl methacrylate polymer, at least one substratum layer adjacent thereto and containing a methyl methacrylate polymer having 15 to 25% free carboxyl groups, and a gelatino silver halide emulsion layer adjacent to said substratum layer.

6. A photographic element which comprises a support having a surface of a substantially fully esterified methyl methacrylate polymer, a substratum layer adjacent thereto containing gelatin and a methyl methacrylate polymer having 15 to 25% free carboxyl groups, and a gelatino silver halide emulsion layer adjacent to said substratum layer.

7. A photographic element which comprises a support having a surface of a substantially fully esterified methyl methacrylate polymer, a first substratum layer adjacent thereto containing a methyl methacrylate polymer having 15 to 25% free carboxyl groups, a second substratum layer adjacent to the first containing gelatin and a methyl methacrylate polymer having 15 to 77% free carboxyl groups, and a gelatino silver halide emulsion layer adjacent to said second substratum layer.

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