This is a continuation-in-part of our application Ser. No. 197,820, filed May 23, 1962 (abandoned).

The invention disclosed in this application relates to copolymers of acrylates, acrylic acid and N-methylol- methacrylamide and aqueous dispersions of copolymers of this type. The invention also relates to leather whose surface has been coated with a copolymer of acrylates, acrylic acid and N-methylolmethacrylamide.

The use of copolymer dispersions produced by the copolymerization of water-insoluble monomers and polymerizable acids, such as acrylic or methacrylic acid, for the finishing of fibrous materials is well known. Films formed by dispersions of this type generally have good adhesion on the fibrous material. It is also well known that dispersions of copolymers in which large quantities of acrylic acid have been incorporated by polymerization can in some cases be made highly viscous by addition of aqueous ammnonia. This possibility of thickening the dispersions is often very useful for the finishing of fibrous materials, because the filling effect and the film forming power increase with rising viscosity, and also because the viscous dispersions have less tendency to penetrate into the fibrous material.

Dispersions prepared in the normal manner from copolymers of water-insoluble monomers and large quantities of acrylic or methacrylic acid are, however, susceptible to the coagulating effect of mechanical and/or thermal stresses and to additions of electrolytes and pigments, and this susceptibility generally increases in proportion to the amount of acrylic or methacrylic acid which has been polymerized into the copolymer. This, therefore, relatively narrow limits set to the proportion of water-soluble monomers, in particular α,β-unsaturated carboxylic acids, polymerized into such copolymer dispersions, within which the dispersions have the minimum stability necessary for storage, transport, an addition of electrolytes, and for processing of machines.

Object of this invention are copolymers from acrylates, acrylic acid and N-methylolmethacrylamide which form stable dispersions in water. A further object of this invention are stable aqueous dispersions of copolymers from acrylates, acrylic acid and N-methylolmethacrylamide. Another object of this invention is the use of aqueous dispersions of copolymers from acrylates, acrylic acid and N-methylolmethacrylamide which are useful for the finishing of fibrous materials, in particular the surface of leather. Another object of this invention is leather whose surface has been improved by treatment with aqueous dispersions of copolymers of acrylates, acrylic acid and N-methylolmethacrylamide. As shown in the examples, another object of the invention is to provide coatings and in particular leather finishes having an improved resistance to acetone and hot plating by treatment with copolymers of acrylates, acrylic acid and N-methylolmethacrylamide. Further objects of the invention will become apparent to those skilled in the art.

It has now been found that the properties of fibrous materials, especially leather, can be improved by treating these materials with aqueous dispersions of copolymers being produced by copolymerizing at a pH value smaller than 5.5 from 60 to 95.5% by weight of an ester of acrylic acid and a saturated alkanol with 1 to 8 carbon atoms, 3 to 30% by weight of acrylic acid, and 0.5 to 10% by weight of N-methylolmethacrylamide.

As shown in the examples it has further been found that copolymers of at least 80% by weight of ethyl acrylate, 1 to 5% of N-methylolmethacrylamide and acrylic acid, films prepared from them exhibit excellent resistance to acetone and hot plating, when the copolymers contain at least 7.5% and particularly from 7.5 to 15% by weight of acrylic acid units. These copolymers are of particular interest in the finishing of leather.

The copolymerization method mentioned above has various advantages. In the first place aqueous dispersions thus prepared have good stability, even when they contain a large proportion of acrylic acid. In addition, finishes on the treated fibrous materials have good resistance to solvents. The copolymer dispersions are new. As described in the following, they can be prepared by copolymerization of the said monomers in aqueous emulsion.

This can be achieved by means of the normal processes of emulsion polymerization, using standard catalysts, emulsifying agents and or protective colloids, and maintaining the pH below 5.5, preferably between 2.5 and 5.

Suitable catalysts are the common peroxide-type compounds, e.g. persulfates as potassium persulfate or ammonium persulfate, and redox systems or mixtures of various catalysts. Suitable emulsifying agents are the common surface-active substances, such as fatty acid salts, alkyl sulfonic acid salts, salts of sulfuric semi-esters of long chain alcohols, etc. These emulsifying agents can be used in mixtures with one another or together with protective colloids.

A particularly advantageous process for the production of these dispersions is to charge a vessel with water, polymerization catalysts, and if necessary, emulsifying agents and other auxiliary materials, and then to add the monomers at a pH value smaller than 5.5 at a rate corresponding to the progress of polymerization. The preferred emulsifying agents for this purpose are ammonium salts and/or alkali salts of sulfuric semi-esters of oxyalkylation products. They are placed in the polymerization vessel either before or simultaneously or in combination with the monomers. Suitable alkali salts are in particular sodium and potassium salts.

"Oxyalkylation products" in the present invention refers to materials which are produced by reaction of ethylene oxide or propylene oxide with higher carboxylic acids, with higher carboxylic acids or their amides or imides and with alkanols or sulfonamides and sulfonimides. Such salts of sulfuric semi-esters are well known emulsifying agents, and one method of producing them is to react saturated or unsaturated fatty acids or fatty acids with at least 12 carbon atoms or resin acids with 5 to 40 mole equivalents of ethylene oxide or propylene oxide, then sulfonate the oxyalkylation products and neutralize wholly or partially with alkali or ammonia. Suitable fatty acids, fatty acids or resin acids are, e.g., coconut oil alcohol,

ABSTRACT OF THE DISCLOSURE

Aqueous leather coating dispersions are prepared from polymers of alkyl acrylates, acrylic acid and N-methylolmethacrylamide. The copolymers are prepared using a critical weight ratio of at least 80% ethyl acrylate and not more than 15% by weight acrylic acid, and 1 to 5% by weight of N-methylolmethacrylamide.

This invention relates to copolymers of ethyl acrylate, acrylic acid, and N-methylolmethacrylamide. These copolymers are prepared by copolymerization of ethyl acrylate, acrylic acid, and N-methylolmethacrylamide. The copolymer dispersions are prepared by the copolymerization of water-insoluble monomers and polymerizable acids, such as acrylic or methacrylic acid, for the finishing of fibrous materials. Films formed by dispersions of this type generally have good adhesion on the fibrous material. It is also well known that dispersions of copolymers in which large quantities of acrylic acid have been incorporated by polymerization can in some cases be made highly viscous by addition of aqueous ammonia. This possibility of thickening the dispersions is often very useful for the finishing of fibrous materials, because the filling effect and the film forming power increase with rising viscosity, and also because the viscous dispersions have less tendency to penetrate into the fibrous material. Dispersions prepared in the normal manner from copolymers of water-insoluble monomers and large quantities of acrylic or methacrylic acid are, however, susceptible to the coagulating effect of mechanical and/or thermal stresses and to additions of electrolytes and pigments, and this susceptibility generally increases in proportion to the amount of acrylic or methacrylic acid which has been polymerized into the copolymer. This, therefore, relatively narrow limits set to the proportion of water-soluble monomers, in particular α,β-unsaturated carboxylic acids, polymerized into such copolymer dispersions, within which the dispersions have the minimum stability necessary for storage, transport, addition of electrolytes, and for processing of machines.

Object of this invention are copolymers from acrylates, acrylic acid and N-methylolmethacrylamide which form stable dispersions in water. A further object of this invention are stable aqueous dispersions of copolymers from acrylates, acrylic acid and N-methylolmethacrylamide. Another object of this invention is the use of aqueous dispersions of copolymers from acrylates, acrylic acid and N-methylolmethacrylamide which are useful for the finishing of fibrous materials, in particular the surface of leather. Another object of this invention is leather whose surface has been improved by treatment with aqueous dispersions of copolymers of acrylates, acrylic acid and N-methylolmethacrylamide. As shown in the examples, another object of the invention is to provide coatings and in particular leather finishes having an improved resistance to acetone and hot plating by treatment with copolymers of acrylates, acrylic acid and N-methylolmethacrylamide. Further objects of the invention will become apparent to those skilled in the art.

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As shown in the examples it has further been found that copolymers of at least 80% by weight of ethyl acrylate, 1 to 5% of N-methylolmethacrylamide and acrylic acid, and films prepared from them exhibit excellent resistance to acetone and hot plating, when the copolymers contain at least 7.5% and particularly from 7.5 to 15% by weight of acrylic acid units. These copolymers are of particular interest in the finishing of leather.

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"Oxyalkylation products" in the present invention refers to materials which are produced by reaction of ethylene oxide or propylene oxide with higher carboxylic acids, with higher carboxylic acids or their amides or imides and with alkanols or sulfonamides and sulfonimides. Such salts of sulfuric semi-esters are well known emulsifying agents, and one method of producing them is to react saturated or unsaturated fatty acids or fatty acids with at least 12 carbon atoms or resin acids with 5 to 40 mole equivalents of ethylene oxide or propylene oxide, then sulfonate the oxyalkylation products and neutralize wholly or partially with alkali or ammonia. Suitable fatty acids, fatty acids or resin acids are, e.g., coconut oil alcohol,
sperm oil alcohol, wax alcohol, sperm oil fatty acid, stearic acid, oleic acid, ricinoleic acid, and abietic acid and fatty products or paraffin wax oxidation. Mixtures of such materials are also suitable. In place of such fatty alcohols or carboxylic acids it is also possible to use amides of carboxylic acids, such as the amides of stearic, oleic, sperm oil or ricinoleic acid, or sulfonamides, such as sulfanilide and cyclohexylsulfamide. It is also possible to use alkali salts or ammonium salts of sulfuric semi-esters, which have been prepared in a similar manner from reaction products of alkylphenols whose straight-chain or branched alkyl residues contain 6 to 20 carbon atoms, with 9 to 60 mole equivalents of ethylene or propylene oxide. Suitable alkylphenols are, e.g., isooctylphenols and isooctylnapthols and dodecyl- and dodocyclophenols and decyl- and docycloxyphthals.

In this preferred method of production, other emulsifying agents, such as alkylsulfonates, sulfuric semi-esters of higher alcohols or non-ionic emulsifying agents, can of course also be employed together with the emulsifying agents mentioned above. In most cases, however, emulsions of copolymers of the indicated composition are obtained and these are less suitable from aspects of application.

"Auxiliaries" in this case refers to the usual materials employed as additions, such as buffer substances and polymerization control substances.

Although the proportion of the monomers mentioned above contained in the copolymers used in accordance with the invention can be varied within a wide range, there are preferred compositions. The proportion of diamine should preferably be between 80 and 95% by weight. Among the acrylates, the esters of alkanols with 2 to 4 carbon atoms are of particular interest, and the copolymers of ethyl acrylate are particularly suitable for the finishing of leather. The proportion of propylene oxide should preferably be 5 to 15% by weight, and the proportion of N-methylmethacrylamide should preferably be 1 to 5% by weight. These percentages refer to the total amount of monomers used for the production of the copolymers. The percentages therefore can also be regarded as being based on the total weight of the copolymer.

Besides these monomers the copolymers may also contain up to 30% by weight, calculated on the total amount of monomers, of other monomers incorporated by polymerization. Examples of such other monomers are methacrylates, maleic and fumaric esters, itaconic esters, acrylonitrile, vinyl acetate, vinyl chloride and vinylidene chloride. The proportion of these monomers should preferably not exceed 25% by weight, as these monomers should not cause any fundamental change of the properties of the copolymers of the three monomers which are absolutely necessary. The polymers may also contain up to 25% by weight, calculated on the quantity of N-methylolacrylamide, or other N-methylol compounds, such as N-methyllacrylamide, N-methylolmaleimide and N-methylolacryloyl urea incorporated by polymerization. Dispersions of polymers containing up to 25% by weight, calculated on the quantity of acryl acid, of other short-chain ethylene-unsatuated mono- and/or dicarboxylic acids, such as in particular methacrylic acid and also maleic acid, fumaric acid, or itaconic acid incorporated by polymerization are also suitable.

In special cases, dispersions of copolymers containing up to 70% by weight of methacrylic acid incorporated by polymerization, calculated on the amount of acrylic acid, are also suitable.

The quantity of ethylenically unsaturated acids incorporated by polymerization should, however, not exceed 15% by weight, calculated on the total amount of monomers.

These copolymers may, of course, be prepared from several of the acrylates mentioned above, for example methyl, ethyl, propyl, isopropyl, n-butyl, iso- butyl, and tertiary butyl acrylates in the proportions indicated above.

Of great interest are also copolymers containing 60 to 96.5% by weight, calculated on the total amount of monomers, of ethyl acrylate, 5 to 15% by weight, calculated on the total amount of monomers of acrylic acid, and 1 to 5% by weight, calculated on the total amount of monomers, of N-methyl methacrylamide and aqueous dispersions containing 5 to 50% by weight of these copolymers. These copolymers may contain up to 25% by weight, calculated on the amount of ethyl acrylate, of other polymerizable ethylenically unsaturated monomers, in particular methacrylates of alcohols with 1 to 4 carbon atoms, methyl, propyl, n-butyl, isobutyl, and tertiary butyl acrylate and acrylonitrile, and also maleic and fumaric esters, itaconic esters, vinyl acetae, vinyl chloride, and vinylidene chloride incorporated by polymerization. Aqueous dispersions of these copolymers can also be used advantageously for the surface coating of leather.

The content of copolymers in the dispersions may vary within wide limits. After preparation of the dispersions it should preferably be between 30 and 50% by weight. When the viscosity is measured at 20°C, the dispersions of the copolymers at pH values between 2 and 6 and a copolymer concentration of 40% by weight show a flow-out rate of 10 to 20 seconds in a Ford cup with an orifice of 4 mm. diameter. Before or during their application, the dispersions may be diluted and/or additional materials may be added if necessary. The degree of dilution depends on the specific application. For the surface coating of leather it may in some cases be sufficient if the mixture used consisting of copolymer dispersion and the usual additional materials has a copolymer concentration of only 1% by weight. Generally speaking, dispersions containing 10 to 20% by weight, calculated on the total weight of dispersion, of copolymer are used for the preparation of mixtures which are suitable for the surface coating of leather and which consist of dispersion and the usual additional materials. In special cases, however, higher concentrations, i.e., up to 50% by weight, or lower concentrations, i.e., down to 5% by weight, of copolymer in the dispersion may be of advantage.

The copolymers themselves are of high-molecular weight and film-forming. They can be characterized by the elongation at rupture of films of the copolymers. Films of the copolymers show an ultimate elongation of 700 to 1000% when measured according to DIN 53371. Copolymers containing 80 to 95% by weight of ethyl acrylate, 5 to 15% by weight of acrylic acid, and 1 to 5% by weight of N-methylolmethacrylamide form from aqueous dispersions containing up to 50% by weight of copolymer, even at room temperature, films with an ultimate elongation of 500 to 800%, measured in accordance with DIN 53371. Such copolymers are of particular interest and are therefore preferred. Surprisingly, those copolymers and films prepared from them which contain at least 7.5% and particularly 7.5 to 15% of acrylic acid units are markedly superior to those which contain only 5% or less of acrylic acid units with regard to resistance to acetone and hot plating.

Films of the copolymers also have a tensile strength of 10 to 100 kg./sq. cm., measured in accordance with DIN 53371. When immersed in water at room temperature for 5 hours, they absorb 1 to 40% of their weight of water. Films of copolymers containing 80 to 95% by weight of ethyl acrylate, 5 to 15% by weight of acrylic acid, and 1 to 5% by weight of N-methylolmethacrylamide show an exceptionally useful water absorption. When immersed for 5 hours in water at room temperature, they absorb 1 to 10 by weight. This is an advantage particularly in the use of the copolymer dispersions for the coating of leather surfaces.

The dispersions are eminently suitable for the perma-
inent finishing of fibrous materials consisting of an arranged or random systems of natural and/or man-made fibers. They are particularly suitable as bonding agents for fibrous webs and felts and for the permanent finishing of textiles, because they yield finishes with exceptionally good resistance to solvents when subjected to a thermal after-treatment. Used as textile finishes the dispersions yield, for instance, finishings which are resistant to solvents, tearing, and wet rubbing.

They are particularly suitable for the surface coating of leather, in which case they are in general applied together with colored pigments and other auxiliary materials usually to the grain side, then dried and plated. The leather finishes thus obtained are characterized by their exceptional lustre, excellent break, elasticity, fastness to hot plating, and resistance to abrasion and acetone. Dispersions thickened with aqueous ammonia solutions are useful mainly for the finishing of split leather.

For the finishing, in particular the surface coating, of leather, aqueous dispersions of copolymers containing 80 to 95% by weight of ethyl acrylate, 5 to 15%, especially 7.5 to 15%, by weight of acrylic acid, and 1 to 5% by weight of N-methylolmethacrylamide are particularly suitable.

In view of the high content of carboxylic groups and acid-sensitive, reactive and cross-linkable N-methylol groups in the polymers, it is surprising that the dispersions have good stability and produce particularly good finishing effects on fibrous materials.

The parts and percentages given in the examples are by weight, unless otherwise indicated.

**EXAMPLE 1**

A mixture containing 150 parts of distilled water, 0.6 parts of potassium persulfate, 1.5 parts of a 35% by weight aqueous solution (1) of the sodium salt of a sulfonated reaction product of isocyanolphenol with 25 mole equivalents of ethylene oxide, prepared in the usual manner, and 24 parts of a 50% by weight aqueous solution (2) of the sodium salt of a sulfonated castor oil, prepared in the usual manner, is heated to 80° C. To this mixture are added simultaneously from separate containers in the course of about 2 hours and at a rate depending on the progress of polymerization and in such a manner that the addition of (a) and the addition of (b) are completed at approximately the same time. There is no accumulation of non-polymerized monomers in the vessel during the process. During polymerization, the pH is smaller than 5.

A solution of 0.2 part of potassium persulfate in 10 parts of water is then added to the reaction mixture, and the temperature is maintained at 80- 90° C. for a further 30 minutes. About 10 parts of water and volatile components of the reaction mixture are then distilled over at 90° C. in a stream of nitrogen, and the mixture is allowed to cool. The dispersion obtained has a pH of 3. 150 parts of this dispersion are mixed with a mixture containing 50 parts of a 10% by weight aqueous casein solution, 25 parts of commercial iron oxide pigment, and 200 parts of water, and the mixture is brushed on grain leather. The coating is dried and then plated at 60-80° C. at a pressure of 100 atm, with the aid of a standard leather plating machine. A leather finish is obtained which has a very good surface lustre, good covering power, abrasion resistance and fastness to hot plating. The leather finish also has substantially good resistance to acetone.

The dispersion can be thickened very extensively by addition of ammonia, and it can be used in the thickened condition for the finishing of split leather.

**EXAMPLE 2**

In a manner analogous to that described in Example 1, 85.5 parts of ethyl acrylate, 13 parts of acrylic acid and 1.5 parts of N-methylolmethacrylamide are polymerized in an aqueous emulsion in such a manner that a 40% by weight aqueous dispersion of a copolymer of these monomers is obtained. The dispersion obtained (referred to in the following as Dispersion D) is very suitable for the surface coating of leather.

A mixture I of

1. (1) 50 parts of Dispersion D
2. (2) 800 parts of water
3. (3) 50 parts of a casein pigment finish C, consisting of 20 parts of commercial iron oxide pigment, 6 parts of a mixture of equal parts of water and sulfated castor oil and 24 parts of a 17% by weight aqueous casein solution having pH 8
4. (4) 100 parts of an emulsion of 40 parts of olive oil, 10 parts of a commercial emulsifying agent and 50 parts of water

is plunge-padded on the grain side of corrected grain side leather.

The leather is then dried and plated. A mixture II of 150 parts of Dispersion D, 400 parts of water, 100 parts of casein pigment finish C, 50 parts of a 77% by weight aqueous casein solution having pH 8, and 5 parts of a mixture of equal parts of water and sulfated castor oil is then applied to the bottomed surface of the leather, again by plunge-paddling. When the leather has been dried again, another coating of mixture II is sprayed on the treated surface. After drying, the coating is fixed by treatment with a fixing solution B containing 300 parts of a 35% by weight aqueous formaldehyde solution, 650 parts of water, and 50 parts of 33% by weight acetic acid.

A mixture III containing 150 parts of a 17% by weight aqueous casein solution having pH 8, 835 parts of water, and 15 parts of a mixture of equal parts of water and sulfated castor oil is then sprayed on the treated surface of the leather. After drying, the coating is again fixed with the fixing mixture B; this is followed by plating.

The leather obtained has a smooth hand and good fastness to wet and dry rubbing. It can be used for the production of shoes, in which application it withstands plating temperatures of at least 150° C.

**EXAMPLE 3**

In a manner analogous to that described in Example 1, a 40% by weight aqueous dispersion of a copolymer is prepared from 88 parts of ethyl acrylate, 7.5 parts of acrylic acid and 4.5 parts of N-methylolmethacrylamide. The dispersion obtained, referred to in the following as Dispersion E, is very suitable for the surface coating of leather.

A mixture I containing 200 parts of Dispersion E, 100 parts of the casein pigment finish C described in Example 2 and 400 parts of water is plunge-padded as an undercoat to the grain side of corrected grain side leather. This is followed by drying and plating.

A mixture II containing 100 parts of the casein pigment finish C described in Example 2, 75 parts of a 17% by weight aqueous casein solution having pH 8, 8 parts of a mixture of equal parts of water and sulfated castor oil, 150 parts of Dispersion E, and 400 parts of water is then applied to the treated surface, again by plunge-paddling.

After drying, another amount of mixture II is sprayed on the treated surface of the leather. The coating thus obtained is fixed by treatment with the fixing mixture B described in Example 2, and then a mixture III containing 20 parts of Dispersion E, 800 parts of water, 180 parts of a 17% by weight aqueous casein solution having pH 8 and 18 parts of a mixture of equal parts of water
and sulfated castor oil is applied by spraying. This coating is treated with a fixing mixture containing 300 parts of a 35% by weight aqueous formaldehyde solution, 650 parts of water, 50 parts of 35% by weight acetic acid and 2.5 parts of chromium-III-acetate. The leather is then dried and plated. The treated leather has exceptionally good resistance to acetone.

EXAMPLE 4

In a manner analogous to that described in Example 1, a 40% by weight aqueous dispersion of a copolymer is prepared from 80 parts of ethyl acrylate, 14 parts of acrylic acid, 4 parts of acrylonitrile and 2 parts of N-methylolmethacrylamide. A dispersion, referred to in the following as Dispersion G, is obtained which is very suitable for the surface coating of leather.

A mixture I containing 50 parts of Dispersion G, 2.5 parts of borax, 970 parts of water, 20 parts of a 20% by weight wax emulsion and 30 parts of a pigment finish containing 10 parts of carbon black, 10 parts of casein and 10 parts of a mixture of equal parts of water and sulfated castor oil is plush-padded on the calf leather. After drying and polishing, another amount of mixture I is plush-padded onto the treated surface of the leather, and then dried in the air. A further amount of mixture I is then sprayed on. The coatings are fixed by treatment with the fixing mixture B described in Example 2, and dried.

A mixture II containing 80 parts of a 20% by weight aqueous casein solution having pH 8, 860 parts of water and 10 parts of a mixture of equal parts of water and sulfated castor oil is then applied by spraying. This coating is also fixed by treatment with fixing mixture B. After drying and glazing, a leather is obtained which has a supple hand, high luster, very fine break and good aging resistance.

EXAMPLE 5

In a manner analogous to that described in Example 1, a 40% by weight aqueous dispersion of a copolymer is prepared from 80 parts of ethyl acrylate, 7 parts of isobutyl acrylate, 3 parts of methyl methacrylate, 7.5 parts of acrylic acid and 2.5 parts of N-methylolmethacrylamide. A dispersion, referred to in the following as Dispersion H, is obtained which is very suitable for the surface coating of leather.

For the undercoat, a mixture I containing 150 parts of Dispersion H, 200 parts of water, 100 parts of the casein pigment finish C described in Example 2 and 50 parts of a commercial aqueous emulsion of a nitrocellulose lacquer is plush-padded on to the grain side of sheepskin tanned with vegetable tannin. After drying, another amount of mixture I is sprayed on.

After drying again, a mixture II containing 100 parts of a commercial aqueous emulsion of a nitrocellulose lacquer containing 13% by weight of non-volatile components and 23 parts of a 30% by weight aqueous formaldehyde solution is applied by spraying. After drying and glazing, a leather is obtained whose treated surface is smooth and glossy and is distinguished by very good rub fastness.

We claim:

1. Aqueous dispersions containing 5 to 50% by weight, calculated on the total weight of the dispersion, of a copolymer containing in polymerized form at least 80% by weight of ethyl acrylate, at least 7.5% by weight and not more than 15% by weight of acrylic acid and 1 to 5% by weight of N-methylolmethacrylamide, the percentages of these monomers being based on the total weight of the copolymer, said dispersions having been prepared by copolymerization of said monomers in an aqueous emulsion while maintaining the pH of the emulsion below 5.5.

2. Leather whose surface has been coated with an aqueous dispersion of a copolymer containing at least 80% by weight of ethyl acrylate, at least 7.5% by weight and not more than 15% by weight of acrylic acid and 1 to 5% by weight of N-methylolmethacrylamide in polymerized form, the percentages being based on the total weight of the copolymer, said dispersions having been prepared by copolymerization of said monomers in an aqueous emulsion while maintaining the pH of the emulsion below 5.5.

3. An aqueous dispersion as in claim 1 wherein said copolymerization takes place at a pH of from 2.5 to 5.

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MURRAY TILLMAN, Primary Examiner.

J. T. GOOLKASIAN, Assistant Examiner.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,361,695
January 2, 1968
Hans Wilhelm et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 13, "equivalents or" should read -- equivalents of --. Column 4, line 72, "1 to 10" should read -- 1 to 10% --.

Signed and sealed this 25th day of November 1969.

(SEAL)
Attest:
Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents