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BUTADIENE-ACRYLATE INTERPOLYMER
TREATMENT OF WOOL

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This invention relates to fiber treatment and particularly to processes of treating wool to reduce substantially the shrinkage of wool, to products obtained by such processes of treatment and to baths utilized in such treatment.

It is known that it is possible to produce non-felting and non-shrinking wool by chlorination or bromination of wool. There have also been described processes of producing non-felting wool by treatment with alcohol solutions of alkalis, by treatment with sulfuryl chloride, nitrosyl chloride, and the like. (However, in this case mixed cotton and woolen goods cannot be treated.)

Treatment with rubber latex in the presence of quaternary ammonium, phosphonium, sulfonium compounds and the application of alkylated methylol melamine in relatively high temperatures have also been described.

In the prior art processes difficulties are encountered, including danger of damage to fibers, reducing wearing qualities and undesirable hand, which are hard to prevent in most of the former processes.

Processes have also been suggested for the use of synthetic resins, such as methacrylate resins, butadiene polymers, etc., for the treatment of a wide variety of fibers. Those suggestions in the art treat all of these polymeric substances as equivalent for all fibers. But investigation proves that such suggestions are erroneous because while such resins and polymers can be applied to wool for example, they are not equally efficacious in effecting a shrink-proofing effect. Effective shrink-proofing requires definite conditions and compositions and the determination of such conditions and compositions is a matter that cannot be predicted with reasonable certainty.

In prior application Serial No. 537,537, filed May 26, 1944, entitled Woolen treatment and products therefor, in the name of John B. Rust, it has been disclosed that no shrink-proofing effect whatever is obtained unless a straight butadiene polymer is used or some polymer in which butadiene is present to a major extent. The present invention is a continuation of the work leading to effect shrink-proofing of fibers specifically wool.

Among the objects of the present invention is a treatment of wool and wool containing fabrics to render them substantially resistant to felting, fulling and shrinkage by relatively simple processes and particularly where the danger of damage to fibers, reducing wearing qualities and undesirable hand are eliminated.

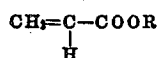
Other objects include the production of treating baths enabling the conditioning of wool to

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produce products of the character set forth above.

Other and further objects and advantages of the present invention will appear from the more detailed description set forth below, it being understood that this more detailed description is given by way of illustration and explanation only and not by way of limitation since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In accordance with the present process the wool either as raw wool, yarn, knit, woven goods or mixed goods is entered into an aqueous conditioning bath containing an interpolymetric butadiene derivative from butadiene and an acrylic derivative, specifically an ester, having the general formula



where R is an aryl or alkyl radical desirably having less than 8 carbon atoms such as methyl, ethyl, propyl, butyl, amyl, benzyl and the like, and exhausting the bath on the fiber. The bath desirably should contain the butadiene interpolymetric in an amount to give, under the conditions of treatment, a wool having from 1% to 25% of interpolymetric based on the weight of the wool. The bath is conditioned by adding to it a sufficiently strong electrolyte to allow the deposition of the interpolymetric butadiene derivative on the wool fibers. It has been found that in such a bath no deposition of the interpolymetric butadiene derivative occurs under ordinary conditions. However, upon addition of an electrolyte, exhaustion of the bath will take place with varying rapidity, depending mainly upon temperature and electrolyte concentration. Without any limitation by way of theoretical considerations, it is believed that reversal of the electrical charge on the colloidal particles of the interpolymetric butadiene derivative takes place on addition of the electrolyte enhancing the affinity of the interpolymetric butadiene derivative for the fiber. The proportion of electrolyte added would be insufficient to account on a theoretical basis for the salting out of the interpolymetric butadiene particles. Thus the effect must be one of electrical charge rather than precipitation by coagulation. When the electrolyte is added to the treated bath there is no coagulation or precipitation even on heating for long periods of time. It is only in the presence of the wool that deposition occurs. This is additional proof that electrical charge of

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the particles is involved rather than a salting effect.

It has furthermore been found that as the acrylic ester content of the interpolymeric butadiene derivative of this invention is increased, shrinkage proofing of the wool decreases rapidly, beyond certain limits. Thus an emulsion of interpolymeric butadiene derivative containing more than 60% of acrylic ester will deposit readily on the wool but no shrinkage proofing is obtained in this manner. However, if the acrylic ester content of the interpolymeric butadiene derivative is decreased, as for example, to 10%, excellent shrinkage proofing is obtained from the treated wool. This effect is both startling and noteworthy since it appears that the shrinkage proofing effect is directly proportional to the butadiene concentration in the interpolymeric material. The effect obtained also varies with the particular acrylic ester utilized. With methyl acrylate, not more than 40% of the interpolymers should be present, while with ethyl acrylate, not more than 50% of the acrylic ester should be present. While those esters in the amounts indicated give a substantial improvement in shrinkage proofing as against untreated wool, the lower esters are not as effective in this direction, and more desirably esters are utilized such as alkyl esters, which contain at least 3 carbon atoms in the alkyl group. For example, butyl acrylate gives a much more pronounced effect than the methyl and ethyl esters, and the butyl acrylate may be present to an amount up to 60% in the interpolymers, without any deleterious effect upon the shrinkage proofing efficiency of the emulsion. In fact, the proportion of acrylic ester within the acceptable ranges as pointed out above, appears to exhibit beneficial effects in certain directions, as for example, in some cases where increased abrasion resistance is obtained in the treated wool.

Consequently the acrylate derivative is utilized with the butadiene in producing the interpolymers, so that the amount of acrylate derivative present is insufficient to interfere with the desired shrink-proofing effect desired while at the same time the amount of acrylate derivative is sufficient to give some special effect on properties in the treated wool which would not be obtainable in its absence.

In the prior art it has been proposed to deposit various synthetic resins and plastics from emulsions onto textile materials. There has been no hint that by varying the composition of such resin emulsions a variation in the physical properties of the treated textile can be obtained.

The electrolyte content may vary over substantial limits but sufficient electrolyte should be present to condition the bath so that the bath, although stable in the presence of wool fibers, will deposit the polymer in the presence of the conditioning electrolyte. Thus the electrolyte content may vary from about 25% to about 500% based on the weight of the interpolymers butadiene derivative present. The following are exemplary; sodium sulfate, sodium chloride, sodium bromide, sodium iodide, sodium sulfite, sodium bisulfate, sodium bisulfite, sodium nitrate, sodium acetate, and the like, or salts of the above using potassium, lithium, caesium and so forth in place of sodium. Salts like zinc chloride may also be used where the coagulation does not appear to be too serious since it occurs in small particulate form and the particles may be redispersed by stirring. As such electrolyte water

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soluble salts may be used, desirably such salts which do not precipitate the polymer, neutral salts, specifically salts of strong bases and strong acids, particularly inorganic salts are preferred. The term "conditioning electrolyte" is used hereinafter to cover such electrolytes which produce the desired deposition of the polymer. It has been found that it is possible to deposit the emulsions of the present invention on wool at pH of seven or even slightly higher. However, it is preferred to operate at a pH of seven or below since under these latter conditions more rapid dispersal is effected.

The operation is desirably carried out at a temperature sufficient to give exhaustion of the bath with the particular emulsion being used. This will vary with different emulsions. While lower temperatures may be used, the operation is desirably carried out at temperature ranges from 40° C. to the boiling point of the bath. The polymer can be applied before or after fulling, weaving, scouring and the like operations. In some cases it can be applied in the dye bath. Mixed goods including wool-cotton, wool-rayon and so forth can be treated by this method without any deleterious effect. If desired the wool may be subjected to a pretreatment, as for example, chlorination or bromination, before being treated in accordance with the present invention. In emulsions containing the acrylate-butadiene interpolymers, the emulsifying agent may be any anionic emulsifying agent which is stable at or below pH 7. Such emulsifying agents are exemplified by sodium lauryl sulfonate, sodium alkyl naphthalene sulfonates, long chain alkyl sodium sulfonates or sulfates, sodium dioctyl sulfosuccinate and so forth. There may also be used neutral non-cationic emulsifying agents such as mannityle monolaurate, the reaction products of protein derivative products with acid chlorides, ethylene oxide reaction products with fatty acids, fatty alcohols and the like.

Emulsions of the interpolymers used in accordance with the present invention are preferably but not necessarily those which have been carried to a 100% polymerization. When 100% polymer is obtained, considerable cross linking occurs in the polymer with consequent insolubility in organic solvents. Thus a type of pre-vulcanization of the polymer has been obtained. It is also possible to vulcanize the interpolymers with mixtures of vulcanizing accelerators such as thiuram disulfide and so forth, vulcanizing agents such as sulfur, dinitrobenzene, alkyl phenol sulfide and so forth, either previously or subsequently to deposition or dyeing into the wool fibers. Antioxidants may also be included.

The treatment of wool fibers is particularly emphasized herein, although animal fibers such as silk and protein fibers such as "Aralac" (a casein fiber) may also be treated in accordance with this invention.

After treatment in accordance with the present invention, the wool is rinsed and dried. Its properties have been altered to such a degree that it no longer has a tendency to felt during washing and consequently is non-shrinking. Although it is not intended that the invention be limited by theoretical considerations, it is thought that the polymeric or interpolymers particles applied as set forth in this description distribute themselves among the fibers of the wool and in some instances fill the interstices of the wool scales, thus preventing an intertwining and consequent felting of the wool. Thus the deposited polymer

or interpolymers would prevent intertwining of the wool fibers and also permit relatively easy slippage of the fibers one on the other.

Exemplifying the present invention the following examples are given:

Example 1.—A series of butadiene-methyl acrylate emulsions was prepared using butadiene and methyl acrylate in the proportions shown in columns A and B of Table I.

Table I

	A	B
	Parts Butadiene	Parts Methyl Acrylate
1	22.5	2.5
2	20.0	5.0
3	17.5	7.5
4	15.0	10.0
5	12.5	12.5
6	10.0	15.0

In all cases the butadiene, which has been passed over calcium chloride, was condensed in pressure reactor cooled to below -5°C . The reactors were kept in the freezing mixture while the methyl acrylate, which had previously been distilled, was added, followed in each case by 50 parts of a buffer solution of pH 11, 3 parts of a 10% aqueous solution of ammonium persulfate, and 25 parts of sodium lauryl sulfate. The buffer solution was made up from 35.8 parts of disodium phosphate and 7.16 parts of trisodium phosphate dissolved in 980 parts of distilled water. The reactor was then taken out of the freezing mixture, closed immediately and was then left standing for about 2 hours in order to allow them to come to room temperature. The reactor was then heated under controlled conditions to 45°C . and agitated continuously. Emulsions #5 and #6 were taken out of the agitator after 24 hours, the reactors with emulsions #1-4 were taken out after 48 hours of agitation. The reactors were allowed to come to room temperature, and opened. None of the six emulsions showed any pressure or foaming, in the case of emulsions #3-6 a slight vacuum was noticed. This indicated complete polymerization in all six emulsions corresponding to a solid content of $33\frac{1}{3}\%$.

Example 2.—The emulsions made according to Example 1 were applied to pieces of woolen flannel $10'' \times 10''$ in size weighing approximately 13 g. Four lengths of $8''$ each were marked on the samples, two in the direction of the warp, two in the direction of the fill, and the lengths were measured.

For each wool sample an amount of emulsion of Example 1 containing a weight of polymer corresponding to 4.5% of the weight of the wool sample to be treated was weighed out. The emulsions were added to 260 parts of water (20 times the weight of the wool) and 2.0 parts of 50% acetic acid were added to the bath. The wool samples, which had been wetted for 10 minutes in water at 27°C . were immersed in the bath and the bath heated to 60°C . in the course of 15 minutes with continuous agitation. In the meantime a weight of anhydrous sodium sulfate corresponding to 26.5% of the weight of the wool (60% Glauber salt based on the weight of the wool) was dissolved in 50 parts of water. When the bath temperature reached 60°C . half of this salt solution was added to the bath, which was kept at 60°C .

with continuous agitation. 15 minutes later the second half of the salt solution was added and the bath kept at 60°C . until exhaustion was indicated by the clearing of the bath. The exhaustion time listed in column C of Table II was counted from the immersion of the wool samples in the bath. The wool samples were taken out of the bath, rinsed with warm water and dried.

Table II

	A	B	C	D		E
	Parts Butadiene	Parts Methyl Acrylate	Exhaustion time, min.	Percent shrinkage		Felting
				Warp	Fill	
1	22.5	2.5	50	32.3	11.2	Bad.
2	20.0	5.0	60	33.9	11.9	Do.
3	17.5	7.5	55	33.9	11.4	Do.
4	15.0	10.0	35	20.8	9.5	Considerable.
5	12.5	12.5	35	33.2	10.3	Bad.
6	10.0	15.0	35	43.5	17.1	Do.
	Untreated sample			42.0	18.9	Very bad.

The wool samples were then washed in a washing machine using 25 parts of powdered soap for 13,000 parts of hot water at 70°C . The samples were washed for 6 hours, rinsed with warm water and dried. The lengths which had been marked on the samples were measured, and the samples inspected for felting. The percentage shrinkage and the felting for these samples and one untreated control sample which had also been washed for 6 hours, are given in columns D and E of Table II. These data show that the treatment with the emulsions improved the shrinking and felting, particularly if the emulsion contains less than 50% methyl acrylate in the polymer, but that the improvement was not as marked as in the next examples. This indicates that better shrink-proofing is obtained with acrylate derivatives where the alcohol radical is relatively large.

Example 3.—A series of butadiene-ethyl acrylate emulsion was prepared using butadiene and ethyl acrylate in the proportions shown in columns A and B of Table III.

Table III

	A	B
	Parts Butadiene	Parts Ethyl Acrylate
1	90	10
2	80	20
3	70	30
4	60	40
5	50	50
6	40	60
7	30	70
8	20	80

In all cases the butadiene which had been passed over calcium chloride, was condensed in pressure reactors cooled to below -5°C . While the reactors were kept in the freezing mixture the ethyl acrylate, which had previously been distilled, was added, followed in each case by 200 parts of a buffer solution of pH 11, 10 parts of 30% hydrogen peroxide and 10 parts of sodium lauryl sulfate. The buffer solution consisted of 35.8 parts of disodium phosphate and 7.16 parts of trisodium phosphate dissolved in 980 parts of distilled water. The reactors were then taken out of the freezing mixture and closed imme-

diately. The reactors were left standing for about 2 hours and allowed to come to room temperature. They were then heated under controlled conditions to 45° C. and agitated continuously. The reactors were taken out after 21 hours, cooled and opened. The reactor containing emulsion #1 showed a considerable amount of pressure and the reactors containing emulsions #2-4 showed a slight pressure on opening. No pressure was noticed when the remaining reactors were opened, i. e., complete polymerization was indicated, and the solid content of emulsions #1-4 was determined and it was found that in spite of the pressure, they had a solid content of 33 1/3% corresponding to complete polymerization.

Example 4.—The emulsions made according to Example 3 were applied to hand knit samples of wool approximately 7" x 5" in size. For each wool sample an amount of emulsion of Example 3 containing a weight of solids corresponding to 6% of the weight of the wool sample to be treated was weighed out. Columns C and D in Table IV show the weights of the wool samples and the respective amounts of emulsion used. The emulsions were added to 200 parts of water and the bath was conditioned with an electrolyte consisting of 1 part of anhydrous sodium sulfate. Then 1 part of 10% sulfuric acid was added to bring the pH of the bath below 7. The wool samples were immersed in the cold bath, which was then heated to 60-70° C. and kept at that temperature. The wool sample was agitated in the bath continuously. After 20 minutes at 60-70° C. the bath was not yet exhausted and another portion of 1 part of anhydrous sodium sulfate was added. A half hour later the baths from emulsions #1 and #2 were clear, i. e., all the latex had been exhausted. The remaining six emulsions cleared up 40 minutes after the addition of the second portion of sodium sulfate. The wool samples were taken out of the bath, rinsed with warm water and dried.

Table IV

	A Parts Butadiene	B Parts Ethyl Acrylate	C Parts Wool	D Parts Emulsion	E Felting and Shrinking
1	90	10	14.81	2.66	Considerable.
2	80	20	14.60	2.63	Bad.
3	70	30	15.62	2.81	Considerable.
4	60	40	15.50	2.79	Do.
5	50	50	15.30	2.75	Do.
6	40	60	10.80	1.94	Very bad.
7	30	70	14.81	2.66	Bad.
8	20	80	14.60	2.63	Do.

The wool samples were then washed in a washing machine using 25 parts of powdered soap for 13,000 parts of hot water at 70° C. The samples were given 6 washings of one hour each, and were rinsed and dried between washings. The extent of the felting and shrinking caused by the washings is shown in column E of Table IV. The emulsions with the lower percentages of ethyl acrylate stood up better than those with the higher percentages. Emulsions with up to 50% ethyl acrylate showed improvement over untreated wool.

Example 5.—A series of butadiene-butyl acrylate emulsions was prepared using butadiene and butyl acrylate in the proportions shown in columns A and B of Table V.

Table V

	A Parts Butadiene	B Parts Butyl Acrylate
1	22.5	2.5
2	20.0	5.0
3	17.5	7.5
4	15.0	10.0

In all cases the butadiene, which had been passed over calcium chloride, was condensed in pressure reactors, cooled to below -5° C. The reactors were kept in the freezing mixture while the butyl acrylate, which had previously been distilled, was added, followed in each case by 50 parts of a buffer solution of pH 11, 2.5 parts of 30% aqueous hydrogen peroxide solution, and 2.5 parts of sodium lauryl sulfate. The buffer solution had been made up by dissolving 35.8 parts of disodium phosphate and 7.16 parts of trisodium phosphate in 980 parts of distilled water. The reactors were then taken out of the freezing mixture, closed immediately and were left standing for about 2 hours in order to allow them to come to room temperature. The reactors were then heated under controlled conditions to 45° C. and agitated continuously for 16 hours. At the end of that period the reactors were taken out of the agitator, allowed to come to room temperature, and opened. Emulsion #1 showed a very slight pressure but no foaming, all the other three emulsions showed a vacuum indicating complete polymerization in all four cases. The solid content of each of these emulsions was, therefore, 33 1/3%.

Example 6.—The emulsions made according to Example 5 were applied to samples of woolen flannel 10" x 10" in size, weighing approximately 13 grams. Four lengths of 8" each were marked on the sample, two in the direction of the warp, two in the direction of the fill.

For each wool sample an amount of emulsion of Example 5 containing a weight of polymer corresponding to 6% of the weight of the wool sample to be treated was weighed out. The emulsions were added to 250 parts of water and the bath was conditioned by the addition of 1.0 part of anhydrous sodium sulfate and 1.0 part of 10% sulfuric acid. The wool samples were immersed in the cold bath, which was then heated to 60-70° C. and was kept at that temperature. The samples were agitated continuously during the application. More anhydrous sodium sulfate was added from time to time in portions of 1.0 or 2.0 parts until the total sodium sulfate in the bath amounted to 7.0 parts. Exhaustion occurred when the bath had been kept at 60-70° C. for 80 minutes. The wool samples were taken out of the bath, rinsed with warm water and dried.

Table VI

	A Parts Butadiene	B Parts Butyl Acrylate	C Percent Shrinkage		D Felting
			Warp	Fill	
1	22.5	2.5	17.6	3.6	Slight.
2	20.0	5.0	15.8	1.6	Do.
3	17.5	7.5	10.4	2.0	Do.
4	15.0	10.0	7.2	0.8	Do.
Untreated sample			40.6	20.2	Bad.

The wool samples were then washed in a washing machine using 35 parts of powdered soap for 18,500 parts of hot water at 70° C. An untreated sample was also washed with this group of samples. All samples were washed for 6 hours, rinsed with warm water and dried. The lengths, which had been marked on the samples, were measured, and the samples inspected for felting. The percentage shrinkage and the extent of the felting are shown in columns C and D of Table VI. The data shown there were corrected by a factor taking care of the difference in the percentage of polymer applied to the wool and of a difference in the washing which was evidenced by the respective controls, so that these data would be comparable to those given in Example 8. The results obtained show that the treated samples were very much superior to the untreated sample.

Example 7.—A series of butadiene-butyl acrylate emulsions was prepared using butadiene and butyl acrylate in the proportions shown in columns A and B of Table VII.

Table VII

	A	B
	Parts Butadiene	Parts Butyl Acrylate
1	12.5	12.5
2	10.0	15.0
3	7.5	17.5
4	5.0	20.0

In all cases the butadiene, which had been passed over calcium chloride, was condensed in pressure reactors cooled to below -5° C. The reactors were kept in the freezing mixture while the butyl acrylate, which had previously been distilled, was added, followed in each case by 50 parts of a buffer solution of pH 11, 3.0 parts of a 10% aqueous solution of ammonium persulfate, and 2.5 parts of sodium lauryl sulfate. The buffer solution had been made up by dissolving 35.8 parts of disodium phosphate and 7.16 parts of trisodium phosphate in 980 parts of distilled water. The reactors were then taken out of the freezing mixture, closed immediately and were left standing for about 2 hours in order to allow them to come to room temperature. The reactors were then heated under controlled conditions to 45° C. and agitated continuously for 24 hours. At the end of that period the reactors were taken out of the agitator, allowed to cool to room temperature and opened. All four showed a vacuum indicating complete polymerization and a solid content of 33½% for each of the emulsions.

Example 8.—The emulsions made according to Example 7 were applied to samples of woolen flannel 10" x 10" in size, weighing approximately 13 grams. Four lengths of 8" each were marked on the sample, two in the direction of the warp, two in the direction of the fill.

For each wool sample an amount of emulsion of Example 7 containing a weight of polymer corresponding to 4.5% of the weight of the wool sample to be treated was weighed out. The emulsions were added to 260 parts of water (20 times the weight of the wool) and 2.0 parts of 50% acetic acid were added to the bath. The wool sample was wetted for 10 minutes in water at 27° C., then immersed in the cold bath, which was

then heated to 60° C. in the course of 15 minutes. In the meantime a weight of anhydrous sodium sulfate corresponding to 26.5% of the weight of the wool (60% Glauber salt based on the weight of the wool) were dissolved in 50 parts of water. When the bath temperature reached 60° C. half of this salt solution was added to the bath, which was kept at 60° C. while the sample was agitated continuously throughout the application. After 15 minutes at 60° C. the second half of the salt solution was added, and the bath kept at 60° C. until exhaustion occurred. This took place after a period of 50-60 minutes counted from the time of the immersion of the sample in the cold bath. The wool samples were taken out of the bath, rinsed with warm water and dried.

Table VIII

20	A	B	C		Felting
	Parts Butadiene	Parts Butyl Acrylate	Percent Shrinkage		
			Warp	Fill	
25	1	12.5	16.3	9.4	Slight.
	2	10.0	18.3	9.6	Do.
	3	7.5	36.3	12.1	Very bad.
	4	5.0	38.8	14.2	Do.
	Untreated sample		40.6	20.2	Do.
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The wool samples together with an untreated sample were then washed in a washing machine using 25 parts of water for 13,000 parts of hot water at 70° C. The samples were washed for 6 hours, rinsed with warm water and dried. The lengths, which had been marked on the sample, were measured and the samples inspected for felting. The percentage shrinkage and the extent of the felting are shown in columns C and D of Table VIII. The data show clearly that up to 60% of butyl acrylate in the polymer emulsions have very good shrink-proofing and felt-proofing properties, while the higher percentages do not seem to have any appreciable effect in this respect.

Having thus set forth my invention, I claim:

1. The method of treating wool which comprises heating the wool in an aqueous emulsion as set forth in claim 2, at a temperature of from 40° C. to the boiling point of the bath.
2. A bath for treating wool to give shrink-proofing with substantially normal hand which comprises an aqueous substantially stable emulsion containing a copolymer of 100% polymerization of butadiene -1.3 and from 10 to 60% by weight of the copolymer of an acrylate ester, the esterifying group being selected from alkyl and aryl groups of not more than 8 carbon atoms, the amount of copolymer being present to give 1 to 25% by weight of copolymer deposition on the wool, a non-cationic emulsifying agent, and at least 25% on the weight of the copolymer of a water-soluble neutral salt of a monovalent salt forming radical as conditioning electrolyte, the pH of the bath being below 7.
3. A bath as set forth in claim 2, in which the copolymer contains not more than 50% of ethyl acrylate.
4. A bath as set forth in claim 2, in which the copolymer contains not more than 60% of butyl acrylate.
5. A bath as set forth in claim 2, in which the copolymer contains not more than 40% of methyl acrylate.

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6. The bath of claim 2, in which the emulsifying agent is anionic.

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