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[54] MANUFACTURE OF PHOTOGRAPHIC PAPER

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[63] Continuation-in-part of Ser. No. 637,903, May 12, 1967, abandoned.

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[58] **Field of Search**.....96/85; 117/34, 76 P

[56] **References Cited**

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[57] **ABSTRACT**

As a binder for pigment, e.g. baryta layers in photographic materials, about 0–75 percent of a conventional protein binder, e.g. gelatin, casein or zein, and about 100–25 percent of a latex of a graft copolymer of 80–99.5 percent of a C_{2-8} alkyl acrylate and 0.5–20 percent acrylonitrile, which latex is obtained by emulsion polymerization of such monomers in the presence of 5–15 percent of PVP and 0.5–2 percent of an anionic surface active emulsifying agent. The binder is used in an amount equal to about 5–25 percent of the pigment. All percentages are by weight and those of the PVP and surface-active agent are with respect to the total weight of monomers present.

7 Claims, No Drawings

MANUFACTURE OF PHOTOGRAPHIC PAPER

The present application is a continuation-in-part of our application Ser. No. 637,903 filed May 12, 1967, now abandoned.

The present invention relates to the manufacture of photographic paper, more particularly to new baryta compositions containing a polymer latex for use in such paper.

Photographic paper generally comprising the following layers:

1. a paper support,

2 a so-called pigment layer usually cast from a dispersion of a pigment such as barium sulphate, titanium dioxide in a hydrophilic or hydrophobic colloid as binding agent,

3. the actual image layer which is light-sensitive layer containing light-sensitive silver halide, or a layer containing development nuclei or substances capable of forming such nuclei in situ, wherein an image can be formed according to the silver complex diffusion transfer process. There may be more than one light-sensitive layer as e.g., in photographic color papers.

In addition to these three principal layers the photographic paper may comprise other layers as well, e.g., a subbing layer improving the adhesion of the light-sensitive layer to the pigment layer, e.g., when the latter contains a hydrophobic binding agent, a filter layer, an antistress layer, an antihalation layer.

Baryta or titanium dioxide layers are applied to paper for rendering the irregular fiber surface uniform and flat. In order to obtain this effect several layers are usually cast. It is impossible indeed to apply light-sensitive emulsion layers or other layers with a uniform thickness and a smooth surface onto a rough and uneven surface. A completely flat surface is required for obtaining photographs or other photographic reproductions of high quality especially with respect to surface gloss, dull spots and uniform blackening.

Pigment layers, usually incorporating barium sulphate as pigment and gelatin as hydrophilic binder, tend to get brittle and to show small fissures upon drying. Moreover, the photographic paper may have a strong tendency to curl. Plasticizers can be added to the pigment suspension to reduce this tendency and at the same time the flexibility is enhanced and the risk of the formation of fissures is considerably diminished.

Low molecular weight plasticizers e.g., glycerol, ethylene glycol and phthalates, have the drawback of migrating into adjacent layers.

The addition of polymer latices as plasticizers to the coating composition of the pigment layer is well known. Unfortunately, these latices which are stabilized hy means of a surface-active compound, and especially pigment suspensions prepared by means of such latices, foam heavily.

If the latices are stabilized by means of a polymeric protective colloid instead of a surface-active compound, the foam formation is considerably lessened. Their synthesis, however, is then more difficult. The particles grow much larger and the distribution thereof in the pigment suspension is worse than with anionic polymer latices.

The present invention provides at least a partial solution to this problem.

According to the invention a photographic paper comprising a paper support, a pigment layer and on such pigment layer a light- sensitive layer or an image-receiving layer for the silver salt diffusion transfer process is characterized in that the pigment layer has been formed by coating the paper support with a suspension of an inert pigment in an aqueous dispersion containing about 5–25 percent by weight of said pigment of a binder comprising about 0 to 75 percent by weight of a protein binder, e.g., gelatin, casein or zein and about 25 to 100 percent by weight of a latex of a graft copolymer obtained by emulsion-copolymerization of 80 to 99.5 percent by weight of an alkyl acrylate, the alkyl group of which contains 2 to 8 carbon atoms, and 0.5 to 20 percent by weight of acrylonitrile, said emulsion polymerization being performed in the presence of 5 to 15 percent weight of poly(N-vinylpyrrolidone),

together with 0.5 to 2 percent by weight of an anionic surface-active compound as emulsifying agent for the polymerization, the percent by weight of the poly(N-vinylpyrrolidone) and of the anionic surface-active compound being calculated on the total weight of monomers present.

The expression "light-sensitive layer" as used in the foregoing definition means light-sensitive silver halide emulsion layers and other light-sensitive layers used in photographic recording and also layers containing photoconductive compounds for use in electrophotography.

Suitable alkyl acrylates are ethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, sec.-butyl acrylate, 2-methyl-1-butyl acrylate, 3-methyl-1-butyl acrylate, 3-pentyl acrylate, n-pentyl acrylate, n-hexyl acrylate, 2-methyl-1-pentyl acrylate, 2-ethyl-1-butyl acrylate, 1,3-diemthyl-1-butyl acrylate, n-heptyl acrylate, n-octul acrylate, and 2-ethyl-1-hexyl acrylate.

Poly(N-vinylpyrrolidones) having molecular weights from 10,000 up to 400,000 are suitable. The molecular weight of the poly(N-vinylpyrrolidone) has no direct influence on the polymerization process, on the stability of the latex formed or on its compatibility with the pigment suspension. Since poly(N-vinylpyrrolidone) with a very high molecular weight causes a certain thickening of the latex, a poly(N-vinylpyrrolidone) with a molecular weight between 10,000 and 100,000 is preferably used.

The emulsion polymerization can be carried out according to known techniques, which are amply described in the examples hereinafter given. The radical initiating agent for the emulsion polymerization can be formed either by thermal decomposition of chemical initiating agents or by the action of a reductor on an oxidizing compound (redox) initiating agents), or by physical action such as the ultraviolet light or other high energy radiation or ultrasonic waves.

The main chemical initiating agents include water-soluble persulphates (ammonium and potassium persulphate), hydrogen peroxide, and 4,4'-azobis(4-cyanovaleric acid), and water-insoluble compounds such as azodiisobutyronitrile, benzoyl peroxide, and chlorobenzoyl peroxide.

Common redox initiating agents include hydrogen peroxide/iron (II) salt, and potassium persulphate/potassium bisulphite.

A survey of initiating agents and their action is given in the book of F. A. Bovey et al.: Emulsion polymerization, Interscience Publishers Inc., New York, 1955, p. 59–63.

In the preparation of the latex for carrying out the present invention the best results are obtained with 4,4'-azo-bis(4-cyanovaleric acid) as initiator.

It has been noticed in the preparation of the polymer latex that the emulsion polymerization of a pure alkyl acrylate along occurs less favorably in the presence of poly(N-vinylpyrrolidone). A part of the poly(alkyl acrylate) formed is lost by precipitation, and the latex particles are rather coarse. Better results with rest to precipitation and particle size are obtained if a small amount of acrylonitrile i.e., 0.5 to 20 percent by weight calculated on alkyl acrylate plus acrylonitrile is added. Larger amounts of acrylonitrile do enhance the quality of the latex, though they start impairing the plasticizing properties of the latex in the pigment suspension.

In order to keep the latex particles as small as possible and to promote thereby their compatibility with the pigment suspension, a small amount (0.5 to 2 percent by weight based on the total weight of monomer present) of an anionic surface-active compounds are is added as emulsifying agent during the polymerication. In this respect in principle all anionic surface-active compounds are suitable. A list of the fundamental classes is given by Laux in "Die grenzflachenaktiven Stoffe," pages 153–242 of Winnacker-Kuchler "Chemische Technologie," Band IV : Organische Technologie, Teil II, Karl Hanser Verlag, Munchen 1960.

Preferred surface-active compounds are the salts of carboxylic acids, such as fatty acids (e.g., alkylcarboxylic acids), fluoroalkylcarboxylic acids, e.g., $Cl(CF_2)_xCOOH$, acylaminocarboxylic acids e.g.,

$$(RCONCH_2COOH)$$
$$\quad\quad|$$
$$\quad\quad CH_3$$

alkyl- or alkaryl-polyethylene oxide carboxylic acids, e.g., $R(OCH_2CH_2)xOCH_2COOH$, alkylaminopropionic acids, alkylpolyamide carboxylic acids, e.g.,

$$RCONHCHCO(NHCHCO)—NHCHCOOH$$
$$\quad\quad\quad|\quad\quad\quad|\quad\quad\quad|$$
$$\quad\quad\quad R'\quad\quad R''\quad\quad R'''$$

This list is incomplete and is merely intended to be illustrative. These surfaces active compounds are converted into soluble salts by the multivalent cations present in the pigment e.g., baryta suspension, and thus become inactive, especially as far as the foaming action is concerned. It can be said that the principal function of the surface-active compound is in the synthesis of the latex and that the role of the poly(N-vinylpyrrolidone) is mainly to serve as a polymeric stabilizer for the latex. Less favorable results, are, however, obtained with a latex, prepared by a method in which the poly(N-vinylpyrrolidone) is only added after the synthesis. The reason for the less favorable results is that in the latter case the poly(N-vinylpyrrolidone) is not chemically bound to the hydrophobic copolymer formed and thus remains soluble in water and not fast to diffusion. When proceeding in accordance with the invention, the poly(N-vinylpyrrolidone) is chemically bound to the hydrophobic copolymer and consequently is no longer soluble in water.

It can easily be provided that the poly(N-vinylpyrrolidone forms a graft copolymer together with the alkyl acrylate and acrylonitrile. As mentioned before the poly(N-vinylpyrrolidone) cannot be washed out anymore in spite of being water-soluble itself. It follows that it is chemically bound to the copolymer formed. Additional evidence follows from the nitrogen content of the copolymer formed. This nitrogen content is always larger than that of the copolymerized acrylonitrile (see example 4).

The use of an anionic surface-active compound has a positive influence with respect to the stability of the latex dispersion. In consequence of the much smaller latex particles and the presence of the anionic emulsifying agent the latex can be stored for several months without coagulation. This stability however is of little practical importance in pigment suspensions for use in photographic papers. In most cases these suspensions are only kept for some hours at the most and usually they are applied immediately they are prepared. Thus an anionic surface-active compound giving increases stability is less critical in this case so that it does not matter when the anionic emulsifying agent reacts with the multivalent cations in the pigment suspension to form an insoluble precipitate.

When preparing a binder latex in accordance with the present invention, only a small amount of anionic emulsifying agent is present. This anionic emulsifying agent is inactivated due to the formation of insoluble salts through reaction with the multivalent cations present in the pigment suspension and in consequence foam formation is avoided or at least reduced as compared with latices stabilized by surface-active compounds. Accordingly the preparation of the pigment suspension is much simplified. Furthermore the deaeration step which was needed in the manufacture of pigment suspensions by the previous method in order to eliminate all air bubbles, is no longer required.

The avoidance or reduction of foam formations is important not only in the preparation of the latices but also is the step of applying the pigmented layer to the photographic paper support, the pigmented composition can be applied from a coating pan and the level of the composition in this pan can be regulated much more accurately in the absence of foam, such regulation being important for obtaining a pigmented layer of uniform thickness.

In addition, to the above advantages, particularly the decrease of foam formation, a latex according to the invention may be manufactured without stabilization of the pigment

suspension by means of dispersing agents. Normally a stabilizing agent such as sodium hexametaphosphate is added when a pigment suspension is manufactured. Indeed when an anionic emulsifying agent is the sole emulsifying agent present, its emulsifying properties are lost through salt formation with multivalent cations of the pigments, and as a result the pigment suspension will precipitate if no stabilizing agent is added. When making a pigment dispersion in accordance with the present invention, wherein polyvinylpyrrolidone is used as the polymeric stabilizer and wherein only a small amount of anionic emulsifying agent is present, this precipitation dies not occur, even in the absence of stabilizing agent. For example, a sufficiently stable baryta suspension can be obtained using a latex with a final pH value between 4.5 and 6.0 without using a stabilizing agent.

According to previous practice, the pigment, e.g., barium sulphate, is dispersed in a binder, usually a protein such as gelatin, casein, or zein, which is used in an amount of from 5 to 25 percent weight calculated on the weight of the pigment. Optimum results however, are obtained with an amount of binding agent of approximately 10 percent by weight. In preparing a photographic paper according to the present invention, the polymer latex can be used in place of part of usual amount of such a binder or the latex can even completely replace such binding agent. Very flexible layers that have hardly any tendency to curl the final photographic paper are obtained when the weight proportion between the solid substance in the latex of the graft polymer and the outer solid substance (if any) in the binder, is approximately 50:50.

A number of specific examples will now be given of methods of preparing binder latices for the pigment layer of photographic paper according to the invention. Although these examples refer particularly to pigment suspensions in which barium sulphate is used as pigment, other inert pigments, e.g., titanium dioxide, can be used as well. When coated on paper supports the pigment layers made of these pigment suspensions are not only suitable as subbing layers for light- sensitive silver halide emulsion layers but also as subbing layers for other light-sensitive layers, e.g., photoconductive pigment layers for use in electrophotography, and layers containing development nuclei in which an image can be formed according to the silver complex diffusion transfer process.

EXAMPLE 1

A 2 liter flask provided with a stirrer, a thermometer, a nitrogen inlet, a reflux condenser and three dropping funnels was used for the preparation. For solutions were prepared:

Solution A

50 g. of poly(N-vinylpyrrolidone) having a molecular weight of approximately 10,000 in 550 ccs. demineralized water.

Solution B

4 g. of sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) in 80 ccs. of demineralized water.

Solution C

300 g. of butyl acrylate and 40 g. of acrylonitrile.

Solution D

3.4 g. of sodium laurate in 60 ccs. of demineralized water.

In the flask 300 ccs. of solution A and the total amount of solution D were brought together. The solution was stirred for 15 minutes at room temperature while a stream of nitrogen was led through. The solution was then heated to 90° C. Subsequently 60 ccs. of solution C were added and as soon as the latter was emulsified, 20 ccs. of solution B were added. The polymerization started immediately and the remainder of solution A, of solution C, and 40 ccs. of solution B were added by means of the dropping funnels. The temperature rose to 92° C, which is the reflux temperature. The addition rate was regulated so that the addition of the three solutions was completed simultaneously. Then the reflux was continued for 5 more minutes whereupon the temperature rose to 97° C. The mixture was stirred for another 10 minutes at 97° C. and the

remaining 20 ccs. of solution B were added. No exothermic reaction could be observed anymore. Heating was continued for 30 minutes at 95°–97° C. The resulting latex was freed from the residual monomer by conducting an airstream at 95°–97 C. and slightly diminished pressure over the latex. The latex was then cooled while stirring. The slightly viscous and bright yellow latex was then filtered. It possessed a concentration of 44 percent by weight.

A foam test was then carried out with the thus formed latex. In a 250 ccs. measure glass provided with a ground stopper 100 ccs. of latex were vigorously shaken by hand 20 times. For comparison a latex of butyl acrylate and acrylonitrile prepared as above but without poly(N-vinylpyrrolidone) was treated in the same way. Immediately after shaking and after 1,2 and 3 minutes respectively the upper level was read. The "foam volume" was obtained by subtracting 100 from this indicated level. The results are shown in the following table.

FOAM VOLUME

		after 1 min.	after 2 min.	after 3 min.
Latex example comparison	70 ccs.	42	20	8
latex	74 ccs.	66	66	64

It appears from the Table that the latex of the graft copolymer prepared in accordance with the invention formed less foam and that the formed foam disappeared considerably faster.

The pigment suspension was prepared as follows: 100 g. of a 50 percent aqueous paste of barium sulphate containing 1 percent of dispersing agent e.g., sodium hexametaphosphate, was suspended in a solution of 45 g. of gelatin in 200 g. of water. The pH was adjusted to 5 by means of citric acid. While vigorously stirring 112.5 g. of the above latex of the graft polymer of butyl acrylate, acrylonitrile, and poly(N-vinylpyrrolidone) was added.

Another foam test was carried out with the thus formed baryta suspension. In a 250 ccs. measure glass provided with a ground stopper, 100 ccs. of baryta suspension were shaken vigorously 20 time by hand. The comparison material was a baryta suspension comprising a latex with anionic emulsifying agent but without protective colloid. The results are shown in the following table:

FOAM VOLUME

		after 1 min.	after 2 min.	after 3 min.
baryta suspension	22 ccs.	20	18	16
comparison material	38 ccs.	38		36

From the baryta suspension prepared in accordance to the invention a layer was coated on a paper web prorate of 30 g. per sq.m., dried and glazed by calendering. Then a light-sensitive silver halide layer was layer was was formed on the baryta layer. The resulting photographic paper possessed excellent properties. Ageing tests did not produce fissures and the photographic paper showed less curling tendency. A stability test was then carried out as follows:

A sufficiently stable baryta suspension with a final pH between 4.5 and 6 was prepared with the above described latex without stabilization of the suspension, e.g., with sodium hexametaphosphate. The same result could not be achieved with a common anionic latex such as a comparison latex prepared without poly(N-vinylpyrrolidone. Two baryta suspensions were composed as follows:

Suspension I

a 50 % by weight aqueous paste of barium *tsulphate*	1,000 g.
gelatin	25 g.
latex according to the invention (40 %)	62.5 ccs.
water	190 ccs.
the pH was adjusted to different values with citric acids	

Suspension II

a 50 % by weight aqueous paste of barium sulphate	1,000 g.
sodium hexametaphosphate 10 % as stabilizing agent	30 ccs.
gelatin	25 g.
latex prepared without poly(N-vinylpyrrolidone	62.5 ccs.
water	190 ccs.
the pH was adjusted to different values with citric acid or sodium hydroxide	

Viscosity measurement of the two baryta suspensions were carried out at different pH values. The results are listed in the following table:

	Viscosity of the baryta suspension in cps.			
	Without stabilizing agent (series I)		With stabilizing agent (series II)	
pH value	Example	Comparison material	Example	Comparison material
5	30	Coagulated	28	10
5.0	35	do		
5.5	30	do	21	12
7.0			21	10
8.5			19	10

Consequently, the latex according to the invention was less dependent on the use of dispersing agents. This allows a broader choice of the viscosity adjustment without need of known thickening agents.

EXAMPLE 2

The process of example 1 was repeated, but a poly(N-vinylpyrrolidone) having a molecular weight of 40,000 was used. A latex with a concentration of 38 percent was obtained. This latex was worked up with a barium sulphate paste in the same way and coated on paper web.

The results obtained with the so prepared photographic paper were favorable

EXAMPLE 3

The process of example 1 was repeated, with the proviso, however, that solution C was replaced by a mixture of 320 g. of butyl acrylate and 15 g. of acrylonitrile. A white easily filterable latex with a concentration of 38 percent was obtained.

When using a baryta paste worked up as in example 1 , a photographic paper showing very good properties was obtained.

EXAMPLE 4

In a 22 liter flask provided with a stirrer, a condenser, a contact thermometer, a dropping funnel, a nitrogen inlet and a heating jacket were placed 720 g. of poly(N-vinylpyrrolidone) having a molecular weight of 10,000 dissolved in 9,900 ccs. of demineralized water and brought to a pH 7 with N-sodium hydroxide. A neutralized solution of 64.8 g. of lauric acid in 850 ccs. of demineralized water was added thereto. The

resulting solution was rinsed for 15 min. with nitrogen while stirring and then heated to 92°–93° C. Subsequently 1,500 ccs. of a monomer solution of 360 g. of acrylontrile and 6,120 g. of butyl acrylate were added. A slight reflux was noticed. After the monomer was emulsified 1,200 ccs. of a 5 percent solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) in demineralized water were added. The polymerization started almost immediately. The remainder of the monomer solution was then added dropwise in 15 minutes. The reflux was considerable at 95°–96° C. When all of the monomer was added, the temperature rose to 97°–98° C. After stirring for another 10 minutes at 97°–98° C, 96 ccs. of a 5 percent solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) in demineralized water were added and the mixture was allowed to polymerize further for 20 minutes at 97° C. The residual monomer was eliminated by conducting an airstream over the latex under slightly reduced pressure. The latex was cooled while stirring and then filtered. Concentration 38 percent. A polymer fraction from the latex was separated by freeze-drying. The polymer was dissolved in butanone and separated again by pouring the butanone solution into a large excess of demineralized water. Upon drying, a nitrogen analysis yielded a content of 2.33 percent. This analysis indicated that grafting on of the poly(N-vinylpyrrolidone) has occurred, since the nitrogen content due to the presence of acrylonitrile in the monomer composition was only 1.32 percent.

This latex was dispersed in the manner of example 1 in a baryta suspension. The resulting suspension was suitable for coating onto paper webs for supporting light-sensitive photographic layers and receiving layers for the silver salt diffusion transfer process.

EXAMPLE 5

In a flask as described in example 1, 50 g. of poly(N-vinylpyrrolidone) having a molecular weight of 10,000 together with 3.4 g. of sodium laurate were dissolved in 600 ccs. of demineralized water. The solution was rinsed with nitrogen for 15 minutes while stirring and thereafter heated to 95° C.

Subsequently 60 ccs. of a monomer mixture of 300 g. of butyl acrylate and 40 g. of acrylonitrile were added. Through a dropping funnel 70 ccs. of a 5 percent solution of the sodium salt of 4,4'-azo-bis (4-cyanovaleric acid in demineralized water were added. The polymerization started immediately. The remainder of the monomer mixture was added dropwise in 5 minutes so that a continuous reflux was noticed. The reaction temperature was 92°–Σ° C. A slight reflux was still observed at 97° C, i.e., 10 minutes after the last amount of monomer had been added. Then another 10 ccs. of the 5 percent solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) were added. The polymerization was continued at 96°–97 C for another 30 minutes The latex was then freed from residual monomer by conducting an airstream over the latex under slightly reduced pressure. While stirring the latex was cooled and filtered.

Subsequently, the latex was worked up with a baryta suspension as described in example 1 and coated on a paper web. The resulting photographic papers showed good properties.

EXAMPLE 6

Four solutions were formed:

SOLUTION A:

50 g. of poly(N-vinylpyrrolidone) having a molecular weight of 40,000 together with 3.4 g. of sodium laurate in 550 ccs. of demineralized water.

Solution B

2.4 g. of sodium bisulphite in 60 ccs. of demineralized water.

Solution C

4 g. of potassium persulphate in 100 ccs. of demineralized water.

Solution D

300 g. of butyl acrylate and 40 g. of acrylonitrile.

An amount of 300 ccs. of solution A and the total amount of solution B were added to in a reaction flask as described in example 1. The mixture was rinsed with nitrogen for 15 minutes while stirring and heated to 85° C.

An amount of 60 ccs. of the monomer mixture D was added and afterwards also 10 ccs. of solution C. A slightly exothermic polymerization started almost immediately. The remainders of solution A and solution D, and 50 ccs. of solution C were added dropwise through separate funnels in approximately 15 minutes. The temperature rose to 89° C. and dropped to 86° C. at the end of the addition. Heating was continued at 84° C. for 10 minutes and 40 ccs. of solution C were added. Stirring was continued for 10 minutes at 87° C. The residual monomer was separated by conducting an airstream over the latex for 10 minutes under slightly reduced pressure.

The white latex was cooled while slowly stirring, and filtered through a nylon cloth. The pH of the latex was 1.7. While thoroughly stirring the pH was then adjusted to 5 by means of sodium hydroxide.

The latex was worked up with a baryta suspension as described in example 1 and applied as baryta layer to a photographic paper support.

EXAMPLE 7

Three solutions were formed:

Solution A

50 g. of poly(N-vinylpyrrolidone) having a molecular weight of 40,000 in 550 ccs. of demineralized water.

Solution B

16 ccs. of a 30 percent aqueous solution of hydrogen peroxide, in 80 ccs. of demineralized water.

Solution C

320 g. of butyl acylate and 38 g. of acrylonitrile.

An amount of 360 ccs. of solution A was brought in the reaction flask as described in example 1 and was stirred for 15 minutes under nitrogen atmosphere and heated to 90° C. Then 60 ccs. of the monomer mixture C were added first and afterwards 20 ccs. of solution B, together with 2 g. of sodium laurate dissolved in 35 ccs. of demineralized water. The polymerization started after 1 minute stirring. The remainder of solution A and of solution C, and 56 ccs. of solution B were added in 25 minutes. The polymerization occurred at reflux temperature (88°–89° C). Heating was continued for another 20 minutes at 89° C. and 20 ccs. of solution B were added. One hour after the addition of the last amount of initiating agent no reflux was observed anymore and the temperature was 92° C. It was then increased to 94° C. and the last traces of monomer were eliminated by conducting an airstream over the latex under slightly reduced pressure.

The latex was dispersed in a baryta suspension as described in example 1 and coated on a paper web.

EXAMPLE 8

A solution of 40 g. of poly(N-vinylpyrrolidone) having a molecular weight of 10,000 in 500 ccs. of demineralized water and 68 ccs. of a 5 percent solution of sodium laurate in demineralized water were brought in a flask as described in example 1. The mixture was first rinsed for 15 minutes with nitrogen and then heated to 83° C.

Subsequently 60 ccs. of a monomer mixture consisting of 40 g. of acrylonitrile and 320 g. of ethyl acrylate were added thereto. As soon as the monomers were emulsified by vigourously stirring, 30 ccs. of a 5 percent solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) in demineralized water were added. The polymerization started within a few moments and subsequently the remainder of the monomer mixture was added in 15 minutes. The temperature rose to 88° C. and later to 93° C. After stirring for another 10 minutes at 93° C., 6 ccs. of 5 percent solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) in demineralized water were added. The mixture was heated for 20 minutes at 95° C. The latex was then freed from residual monomer by blowing an airstream over the latex under slightly reduced pressure. The

bright white latex was cooled while stirring to room temperature. Concentration: 40 percent. The latex was worked up in a photographic baryta layer as described in example 1.

EXAMPLE 9

Four solutions were prepared:
Solution A

50 g. of poly(N-vinylpyrrolidone) having a molecular weight of 10,000 in 550 g. of demineralized water.
Solution B

4 g. of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) in 60 ccs. of demineralized water.
Solution C

3.4 g. of sodium laurate 60 ccs. of demineralized water.
Solution D

340 g. of butyl acrylate and 17 g. of acrylonitrile.

An amount of 300 ccs. of a solution A together with the total amount of solution C was brought in a reaction flask as described in example 1. The mixture was rinsed with nitrogen for 15 minutes and then heated to 90° C. Subsequently 60 ccs. of solution D were added and emulsified by stirring vigorously. After addition of 20 ccs. of solution B the polymerization started almost immediately. The remainder of solution A, 40 ccs. of solution B and the remainder of solution D were then added dropwise and simultaneously in 5 minutes from 3 dropping funnels. The polymerization was very exothermic and the temperature rose to 98° C. Stirring was continued for another 5 minutes at 98° C. and the remaining amount of solution B was added dropwise. The mixture was then left polymerizing for another 30 minutes at 97°–98° C. and thereupon the latex was freed from residual monomer by blowing an airstream over the latex under slightly reduced pressure. The mixture was then cooled. A white latex with a concentration of 38 percent was obtained. The latex was worked up with a baryta suspension, as described in example 1.

EXAMPLE 10

An amount of 40 g. of poly(N-vinylpyrrolidone) having a molecular weight of 10,000 was dissolved in 550 ccs. of demineralized water in a flask as described in example 1 and 72 ccs. of a 5 percent solution of sodium laurate in demineralized water were added thereto. The solution was rinsed with nitrogen for 15 minutes while stirring and then heated to 85° C, whereupon 60 ccs. of ethyl acrylate were added. As soon as the monomer was emulsified, 36 ccs. of a 5 percent solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) in demineralized water were added. The polymerization started immediately and the temperature rose to 89° C. Another 300 g. of ethyl acrylate and 20 g. of acrylonitrile were added dropwise in 15 minutes, whereby the temperature rose to 95° C. The mixture was stirred for another 10 minutes at 95° C. and another 9 ccs. of the 5 percent solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) in demineralized water were added. The mixture was left polymerizing for 20 minutes at 95° C. The residual monomer was removed by blowing an airstream over the latex under slightly reduced pressure. The latex was cooled while stirring. A well filterable latex was obtained, which was worked up in a photographic baryta layer as described in example 1.

EXAMPLE 11

A solution of 40 g. of poly(N-vinylpyrrolidone) 5 percent a molecular weight of 10,000 and 4 g. of sodium laurate in 600 ccs. of demineralized water were added to a reaction flask as described in example 1. The solution was rinsed for a short time with nitrogen and heated to 90°–92° C. Subsequently 70 ccs. of a monomer mixture of 280 g. of 2-ethyl-1-ethyl-1-hexyl acrylate and 80 g. of acrylonitrile were added. As soon as the monomer was emulsified, 65 ccs. of a 5 percent aqueous solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) were added. A slightly exothermic polymerization started after approximately 1 minute. The remaining amount of the monomer mixture is added in 15 minutes. Five minutes after all of the monomer had been added, another 7 ccs. of 5 percent solution of initiating agent were added. Polymerization was continued another 20 minutes at 92° C. After the polymerization the residual monomer was removed from the latex by blowing an airstream over the latex under slightly reduced pressure at 93° C. After demonomerization the latex was cooled while stirring. Approximately 1,000 ccs. of latex with a concentration of 38 percent were obtained. The latex was used in the preparation of a pigment suspension containing barium sulphate, as in example 1.

We claim:

1. A photographic paper of the type comprising a paper support, a pigment layer, and an image layer coated over said pigment layer, characterized in that the pigment layer has been formed by coating the paper support with a suspension of an inert pigment in an aqueous dispersion containing about 5–25 percent by weight of said pigment of a binder comprising about 0–75 percent of a protein binder and 25 to 100 percent by weight of a latex of a graft copolymer obtained by emulsion copolymerization of 80 to 99.5 percent by weight of an alkyl acrylate, in which the alkyl group contains two to eight carbon atoms, and 0.5 to 20 percent by weight of acrylonitrile, said emulsion polymerization being performed in the presence of 5 to 15 percent by weight of poly(N-vinylpyrrolidone), together with 0.5 to 2 percent by weight of anionic surface-active compound as emulsifying agent for the polymerization, the percent by weight of said poly(N-vinyl-pyrrolidone) and of said anionic surface-active compound being calculated on the total weight of monomers present.

2. A photographic paper according to claim 1, wherein the inert pigment is barium sulphate.

3. A photographic paper according to claim 1, wherein the graft copolymer is obtained by emulsion copolymerization of butyl acrylate and acrylonitrile in the presence of poly(N-vinylpyrrolidone).

4. A photographic paper according to claim 1, wherein the graft copolymer is obtained by emulsion copolymerization of ethyl acrylate and acrylonitrile in the presence of poly(N-vinylpyrrolidone).

5. A photographic paper according to claim 1, wherein the graft copolymer is obtained by emulsion copolymerization of 2-ethyl-1-hexyl acrylate and acrylonitrile in the presence of poly(N-vinylpyrrolidone).

6. A photographic paper according to claim 1, in which the binder comprises 50 percent by weight of gelatin and 50 percent by weight of said graft copolymer.

7. A preparation method of a photographic light-sensitive paper comprising applying first to a paper support a baryta coating composition and secondly a light-sensitive silver halide emulsion, characterized in that the baryta coating composition comprises a suspension of barium sulphate in an aqueous dispersion containing about 5–25 percent by weight of said pigment of a binder therefor, the binder comprising about 0–75 percent of protein binder and 25 to 100 percent by weight of latex of graft copolymer obtained by emulsion copolymerization of 80 to 99.5 percent by weight of an alkyl acrylate, in which the alkyl group contains two to eight carbon atoms, and 0.5 to 20 percent by weight of acrylonitrile, said emulsion polymerization being performed in the presence of 5 to 15 percent by weight of poly(N-vinylpyrrolidone) together with 0.5 to 2 percent by weight of an anionic surface-active compound as emulsifying agent for the polymerization, the percent by weight of said poly(N-vinylpyrrolidone) and of said anionic surface-active compound being calculated on the total weight of monomers present.

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