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3,093,609

BINDER DISPERSION FOR BEATER SATURATION PROCESSES

David A. Feigley, Jr., and Leonard N. Ray, Jr., Lancaster, Pa., assignors to Armstrong Cork Company, Lancaster, Pa., a corporation of Pennsylvania

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This invention relates generally to aqueous binder dispersions and more particularly to aqueous dispersions of organic binders which are particularly suitable for the deposition of the binder onto papermaking fibers suspended in water. The invention also relates to the use of particular aqueous organic binder dispersions in the deposition of the binder onto papermaking fibers in a water suspension. This application is a continuation-in-part of application Serial No. 794,867, filed February 24, 1959, now abandoned.

The invention contemplates an aqueous dispersion of an organic binder in particulate form, the dispersion containing a non-cationic emulsifying agent selected from the group consisting of sulfonated anionic agents and nonionic agents. In addition to one or more of these emulsifying agents, the dispersion of the present invention must also contain about 2–20 parts by weight based on 100 parts by dry weight of the binder of a water-soluble salt of an aliphatic polycarboxylic acid containing at least 36 carbon atoms.

The above-described binder dispersion is useful as a kind of universal dispersion or latex for depositing the binder content thereof onto papermaking fibers, in particular, while the fibers are dispersed in water. It has been unexpectedly discovered that these organic binder dispersions containing a mixture of a non-cationic emulsifying agent and the described aliphatic polycarboxylic acid salt will allow the deposition of an extraordinarily wide variety of organic binders onto papermaking fibers with few, if any, additional treating steps being necessary.

The fibers on which the binder is to be deposited may be asbestos, glass, mineral wool, animal hair, synthetic fibers such as nylon, and mixtures thereof. Cellulosic fibers may be used such as kraft stock, rag stock, soda, sulfate, ground-wood, sulfite stock, and alpha pulp. Other forms of fibrous cellulose such as hydrated cotton linters may be used as may be fibers from other sources such as jute, hemp, sisal, strings, chopped canvas, and other materials either cellulosic or non-cellulosic, organic or inorganic. In the case of cellulosic stocks, it will be found that the binder dispersions of the present invention allow the deposition on the fibers of binders such as polytetrafluoroethylene, which can be made to deposit on such fibers by means of other processes only with great difficulty. Furthermore, the binder dispersions of the present invention allow the deposition of binder on mixtures of fibers, such as an asbestos-cellulose fiber mixture, which normally present difficulty during attempts to deposit thereon such binders as synthetic rubbers, and synthetic thermoplastic resins.

In copending application Serial No. 681,860, now Patent No. 2,940,892 there is described a process and product wherein chrysotile asbestos fibers are reacted with soaps of carboxylic acids containing at least 10 carbon atoms. These soaps include the polycarboxylic acid soaps containing at least 36 carbon atoms as defined in the present case. However, the process contemplated in the copending application is not concerned with the deposition of a binder onto the asbestos fibers, but instead, is concerned with varying the characteristics such as drainage time of the asbestos fibers per se. The present case, on the other hand, is concerned with the modification of

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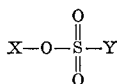
binder dispersions in order to render those dispersions suitable for deposition of the binder content thereof onto any type of papermaking fibers with little or no additional treatment. Hence the present application is concerned with a novel binder dispersion and the use of that dispersion with fiber slurries, while the aforesaid copending application deals with a means for changing the characteristics of the fibers in asbestos slurries without reference to any binder.

The binder dispersions contemplated by the present invention are those dispersions wherein the binder is in the form of small particles (0.05–200 microns) suspended in an aqueous medium initially by means of the usual emulsifying or dispersing agents which are anionic or nonionic in nature. These dispersions or latices may contain as the binder component thereof bituminous particles such as asphalt, tars, and pitches, and bitumens. The binder may also constitute wax particles wherein the wax is a paraffin, carnauba, montan, petrolatum, microcrystalline, or amorphous petroleum wax, or the chlorinated waxes. Any of the forms of rosin may be used as a binder in the present invention. Synthetic rubber and natural rubber latices are also contemplated. Typical of these synthetic rubbers are the products known as GR-S (SBR) which are copolymers of butadiene and styrene containing about 50% to about 70% by weight butadiene. There may also be used the Buna N's or Hycars (NBR) which are copolymers of butadiene and acrylonitrile containing about 50% to about 80% butadiene. The neoprenes may also be used. The neoprenes are polymers of 2-chloro-butadiene-1,3, which polymers are also known as polychloroprenes. If desired, homopolymers of butadiene may be employed as well as homopolymers and/or copolymers of butadiene homologues such as isoprene. These synthetic rubbers may be more specifically designated as rubberlike polymers of butadiene, isoprene, and chloroprene, and rubberlike copolymers of butadiene or isoprene with copolymerizable vinyl compounds such as styrene and acrylonitrile. The polymers and copolymers need not be rubbery in nature in that they may contain a major amount of such copolymerizable ingredients as styrene. The binder dispersions of the present invention also include the thermosetting resins such as the phenol-aldehyde resins, including particularly the phenol and alkyl-phenol-formaldehyde molding resins. The thermosetting resin dispersions also include alkyd resins, urea-aldehyde resins, non-cationic melamine-formaldehyde resins and the various alkyl- or alcohol-reacted urea-formaldehyde resins and melamine-formaldehyde resins. The invention also contemplates use of binder dispersions wherein the particles are of a thermoplastic resin such as any of the polyvinyl resins, the polystyrenes, the polyacrylates, and the polymethacrylates, the polyvinyl esters, for example, the copolymer of vinyl chloride and vinyl acetate, polyvinyl acetal, polyvinyl alcohols, and copolymers of vinyl chloride with a wide variety of material such as styrene, acrylic acid esters, acrylonitrile, acrylamide, and the like. Also included within the scope of the present invention are those binder dispersions of the thermoplastic phenol-aldehyde resins, including phenol-acetaldehyde and phenol-furfural resins and the corresponding resins obtained from cresols and other alkyl phenols. The binders may also be of the oil-modified phenol-formaldehyde type. The esters of rosin with polyhydric alcohols, the coumarone resins, the polyindene resins, and the coumarone-indene resins are also included as are the vinyl acetylene resins. There may also be used binder dispersions of the polymerized, halogenated, unsaturated hydrocarbons such as, for example, polytetrafluoroethylene, called "Teflon." So long as the binder dispersion contains the binder in water-insoluble, particulate form suspended in an aqueous medium, the present invention contemplates the rendering

of that binder suitable for ready deposition onto any paper-making fibers in an aqueous slurry.

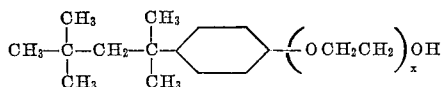
The binder dispersions as described above must all contain a sulfonated anionic or a nonionic emulsifying, dispersing, or wetting agent, or a mixture thereof. Cationic

The term sulfonation is frequently used to designate the reaction of sulfuric acid with organic compounds. The term covers both the true sulfonates and the sulfates, and that is the meaning to be used herein. The general formula for these sulfonates may be stated as



where X is a hydrophilic radical such as H, Na, or K, and Y is a hydrophobic radical such as a hydrocarbon radical, or an ether, amide, or ester radical nonsoluble in water. As examples of the sulfonate anionic agents, there may be mentioned sulfated aliphatic compounds such as sodium lauryl sulfate and the sulfates of higher secondary alcohols, and sulfonated castor oil, sulfonated products such as sodium keryl benzene sulfonate, sodium isopropyl naphthalene sulfonate, esters of sulfocarboxylic acids such as esters of sodium sulfoacetate, dialkyl sulfosuccinamates, disodium monoalkyl sulfosuccinamates, amides of sulfocarboxylic acids such as sodium sulfosuccinamates, sulfonate lignin, the various salts of alkyl aryl sulfonates in general, and so forth. The nonsulfonated anionic emulsifying agents, such as the fatty acid soaps, are excluded from the scope of the present invention, since their presence in the final binder dispersion along with the polycarboxylic acid salts, to be subsequently described, actually retards the deposition of the binder onto the papermaking fibers.

Typical of the nonionic emulsifying agents are the polyhydric alcohol esters and ethers such as the polyethylene glycol-substituted maleic acid esters, the mannitan and sorbitan monoesters of higher fatty acids such as palmitic, stearic, and oleic acids, and their ethylene oxide condensation products, and the aryl-alkyl polyether alcohols which frequently have the formula:



wherein x is a number from 5 to 15.

It is apparent from the above that the present invention contemplates that the binder system contain any of the organic emulsifying, dispersing, or wetting agents so long as those agents are either sulfonated anionic agents or nonionic agents of the group consisting of esters, ethers, and amides, or both.

The remaining ingredient present in the binder dispersion is a water-soluble salt of an aliphatic polycarboxylic acid containing at least 36 carbon atoms. These acids are best illustrated by the dimerized and trimerized fatty acids which are readily available in commerce. These acids are prepared by the thermopolymerization of drying oil acids carried out in a pressure vessel in the presence of water in the form of steam. The resulting compositions generally contain on the average about 3% monomer, 75% dimer, and 22% trimer. Such a product is known as dimerized fatty acids and will generally have an iodine value of approximately 90, and an acid number of approximately 190. The dimerized acid itself is essentially a 36-carbon dicarboxylic acid obtained by dimerization of the linoleic acid of soya, cotton seed, corn, and linseed oils of commerce. The product is frequently referred to as dilinoleic acid. This dimerized acid product may be purchased under the name "Empol 1022." It is apparent that the dimerized acids and the trimerized acids resulting from the above-described pressurized process may be

separated or further concentrated as desired. Thus the trimer acid may be purchased as such. The trimer acid is a 54-carbon acid and contains a plurality of carboxylic acid groups; the trimer acid is preeminently suitable in the present invention. As a further variation on the dimer and trimer acids, any residual unsaturation in the carbon chain may be eliminated by hydrogenation. The hydrogenated dimer acid may be purchased under the name "Emery 3020-S"; the predominantly straight trimer acid may be purchased under the name "Emery 3055-S." These are the polymerized long chain fatty acids containing a plurality of polycarboxylic acid groups and containing at least 36 carbon atoms which are to be added in the form of their salts to the binder dispersion containing one of the above-described emulsifying agents.

The presence of the long chain polycarboxylic acids is critical to form a dispersion which will efficiently deposit the binder content thereof onto papermaking fibers. In the absence of the polycarboxylic acid salt in the binder dispersion, the binder content often simply deposits unevenly, or coagulates in the water when the dispersion is poured into a fiber-containing slurry. With some slurries, the binder will deposit readily, but the resulting slurry of coated fibers is too slow-draining to be used in paper-making processes. The dispersion must also contain an emulsifying agent different from the polycarboxylic acid salts, as described earlier, since the polycarboxylic acid salts as such are generally not sufficiently stable against precipitation by the polyvalent metal ions normally present in an aqueous system. Hence the binder dispersions of the present invention demand the presence of both the described emulsifying agent and the polycarboxylic acid salt if the dispersion is to be suitable for the purposes intended. The present dispersions may be called two-part dispersion systems in that they contain, in addition to the binder, (1) one or more emulsifying agents as defined, and (2) the polycarboxylic acid salt.

The amount of the polycarboxylic acid salt to be added to the dispersion will be in the range of about 2-20 parts by weight, and preferably 2-8 parts by weight, of the polycarboxylic acid salt per 100 parts by dry weight of the binder itself. If the amount of the polycarboxylic acid salt is less than about 2 parts per 100 parts of the binder, the amount is too small to be effective. On the other hand, if amounts of the carboxylic acid salt greater than about 20 parts by weight per 100 parts by weight of the binder are used, the binder dispersion becomes gelatinous, viscous, and difficult to handle and disperse throughout the slurry.

Use of the binder dispersions of the present invention allows the deposition of relatively large amounts of binder onto papermaking fibers. For example, 10-80% by weight binder is readily deposited onto asbestos fibers by the mere addition of the requisite amount of the binder dispersions of the present invention to an asbestos slurry. Simple agitation is all that is needed to complete the deposition. When cellulosic fibers are used, it is preferred that they be pretreated with a small amount of papermaker's alum. The amount of alum to be used will generally be in the range of about 1-10% by weight alum based on the weight of the fibers to be treated. The alum pretreatment is not necessary if the cellulosic fibers have been refined to a low freeness.

The slurry of fibers to which is to be added the binder dispersions of the present invention may be formed in known manner. The fibers are added to sufficient water in a chest or other convenient container in an amount that the resulting slurry contains about 0.3-3% by weight fibers. The preferred consistency of the slurry is about 1% by dry weight fiber based on the total weight of the slurry at the time of addition of the dispersion. This concentration may be varied during mechanical refining, if any, in a beater, Jordan engine, disc refiner, or the like whereby there is produced a slurry wherein the length and diameter of the fibers have been reduced the desired

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degree. Once the consistency of the slurry has been adjusted to the preferred consistency, for example, 1%, the binder dispersion of the present invention is simply poured into the slurry, usually with mere agitation.

The resulting slurry of binder-coated fibers is then formed into a product such as a sheet either on conventional papermaking equipment such as a Fourdrinier wire or cylinder machine, or in shaped molds which allow the draining of the water while retaining the binder-coated fibers. Papers and felts containing one or more of any of the various papermaking fibers bonded together with one or more of any of a wide variety of binders may thus be prepared. The papers may be suitable as toilet tissue, writing papers, or wrapping papers. The felts may be suitable as backing for linoleum and plastic flooring, or as backing for countertop and other surface covering materials. Many of the products prepared by the present process are useful as gasketing materials for a wide variety of applications. For example, the polytetrafluoroethylene-coated asbestos fibers serve as an excellent chemical-resistant gasket.

The following examples illustrate several embodiments of the invention. All parts are by weight unless otherwise stated.

Example 1

Into 3850 parts of water was placed 38.5 parts crocidolite asbestos fibers, and the slurry was beaten for ten minutes in a laboratory beater. The drainage time of the beaten slurry was 345 seconds. To the slurry was added 1.35 parts papermaker's alum; the drainage time remained unchanged.

To 115 parts of a polytetrafluoroethylene (Teflon) dispersion containing 33.5% by weight solids in an aqueous medium and containing as a nonionic emulsifying agent 1.35% by weight of an alkylated aryl polyether alcohol was added 30.5 parts of a 16% by weight solution (4.9 parts dry basis) of the potassium salt of a dimerized acid (dilinoic acid). The salt was stirred into the polytetrafluoroethylene dispersion.

The dimerized acid salt-treated binder dispersion was then poured into the above-described asbestos slurry. The polytetrafluoroethylene smoothly and evenly deposited onto the asbestos fibers leaving a clear, white water. The drainage time of the polytetrafluoroethylene-coated asbestos fibers was 27 seconds. A strong, inert sheet was formed from the coated fibers by pouring the slurry into a laboratory mold having a wire screen at the bottom thereof. The sheet was subsequently formed into a chemical-resistant sheet suitable for gasketing use by pressing the sheet and sintering it at a temperature of 700° F.

Example 2

Example 1 was repeated save that the asbestos used was Canadian chrysotile asbestos which was passed through a Jordan engine; the drainage time was 390 seconds. Slurry containing 38.5 parts chrysotile was pre-treated with 1.9% papermaker's alum on the weight of dry asbestos.

The polytetrafluoroethylene dispersion in the amount of 115 parts was treated by the addition of the 16% dimer salt solution in amounts sufficient to place into the dispersion 4.9 parts of the salt on a dry basis.

The drainage time of the resulting polytetrafluoroethylene-coated asbestos fibers was 52 seconds. A strong sheet was formed therefrom.

Example 3

A sheet was prepared as in Example 1 with the following ingredients:

Ingredients:
Chrysotile asbestos ----- 40 parts.
Water ----- 4,000 parts.
Papermaker's Alum ----- 2 parts.
Asphalt emulsion, 60% by weight solids ----- 24 parts (dry basis).

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Potassium salt of dimerized acid (16% solution) ----- 1.6 (dry basis).
Drainage time ----- 55 seconds.

The dimer acid soap was added to the asphalt emulsion which was stabilized with a sulfonated anionic agent which was sulfonated lignin.

The white water was clear and a strong sheet resulted.

Example 4

A sheet was formed as in Example 1 with the following ingredients:

Ingredients:

Chrysotile asbestos ----- 40 parts.
Water ----- 4,000 parts.
Papermaker's alum ----- 2 parts.
Polyvinyl chloride Latex, 56% by weight dispersion... 30 parts (dry basis).
Potassium salt dimerized acid 1.6 parts (dry basis).
Drainage time ----- 95 seconds.

The polyvinyl chloride latex contained as an emulsifying agent sodium isopropyl naphthalene sulfonate.

An excellent sheet resulted.

Example 5

The following two runs were made to illustrate the great improvement in drainage time conferred on a coated fiber slurry by use of the dispersion of the present invention. The following are the ingredients.

Ingredients	Run A	Run B
Puget Sound sulfite ----- parts	40	40
Water ----- do	4,000	4,000
Papermaker's alum ----- do	1	1
Polyvinyl chloride latex, 56% dispersion containing sodium decyl benzene sulfonate ----- do	10	10
Potassium salt of dimerized acid ----- do	1.6	1.6
Drainage time ----- seconds	150	55

¹ Dry basis.

The only difference between runs A and B above was the addition of the potassium salt of the polycarboxylic acid to the binder dispersion prior to the addition of the resulting dispersion to the fiber slurry. Where the polycarboxylic acid salt is left out of the binder dispersion, as in run A, the resulting drainage time is approximately 300% greater than when the acid salt is included in the dispersion.

Example 6

Runs were made as in Example 1 with the following ingredients:

Ingredients	Run A	Run B
Puget sound sulfite, parts -----	40	40
Water, parts -----	4,000	4,000
Alum, parts -----	1	1
Asphalt emulsion, 60% dispersion containing sulfonated lignin, parts -----	18	18
Potassium salt of dimerized acid, 16% solution, parts -----	1.6	1.6
Drainage time, seconds -----	145	80

¹ Dry basis.

Again, the only difference between run A and run B was the addition of the polycarboxylic acid salt to the binder dispersion.

Example 7

A sheet was made as in Example 1 with the following ingredients:

Ingredients:

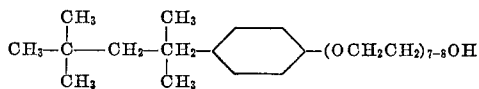
Cottonades ----- parts ----- 40
Water ----- do ----- 4,000
Alum ----- do ----- 1
Phenolic dispersion ----- do ----- 40

Potassium salt of trimerized acid, 16% solution -----	parts--	1.5
Drainage time -----	seconds--	15

The phenolic dispersion had the following formula:

Ingredients:	Parts
Water -----	34
Phenol-formaldehyde resin, less than 200 mesh, U.S. Standard, water-insoluble, alcohol-solu- ble, heat-advancing -----	5
Non-ionic dispersing agent ¹ -----	1

¹ See the following formula:



We claim:

1. An aqueous dispersion of an organic binder in particulate form containing an emulsifying agent selected from the group consisting of sulfonated anionic agents and nonionic agents, and containing in addition thereto about 2-20 parts by weight based on 100 parts by dry weight of said binder of a water-soluble salt of an aliphatic polycarboxylic acid containing at least 36 carbon atoms.
2. A dispersion according to claim 1 wherein said polycarboxylic acid comprises dilinoleic acid.
3. A dispersion according to claim 1 wherein said polycarboxylic acid comprises a trimer acid.
4. An aqueous dispersion according to claim 1 wherein said organic binder comprises a synthetic rubber.

5. An aqueous dispersion according to claim 1 wherein said organic binder comprises a synthetic thermoplastic resin.

6. An aqueous dispersion according to claim 5 wherein said synthetic thermoplastic resin comprises polytetrafluoroethylene.

7. An aqueous dispersion according to claim 1 wherein said polycarboxylic acid salt is present in an amount of about 2-8 parts by weight per 100 parts by dry weight of said binder.

8. An aqueous dispersion according to claim 1 wherein said organic binder comprises an asphalt.

9. An aqueous dispersion according to claim 1 wherein said emulsifying agent is a sulfonated anionic agent and said polycarboxylic acid is a dimerized acid.

10. An aqueous dispersion according to claim 1 wherein said emulsifying agent is a nonionic agent and said polycarboxylic acid is a dimerized acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,450,579	Brown -----	Oct. 5, 1948
2,473,798	Kienle et al. -----	June 21, 1949
2,657,991	Walsh -----	Nov. 3, 1953
2,731,481	Harrison -----	Jan. 17, 1956
2,769,713	Wilson -----	Nov. 6, 1956
2,772,970	Feigley -----	Dec. 4, 1956
2,786,759	Feigley -----	Mar. 26, 1957
2,876,203	Miller et al. -----	Mar. 3, 1959
2,940,892	Feigley et al. -----	June 14, 1960