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DRYING POLYACRYLATES

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The present invention relates to the drying and doctoring of polyacrylate salts in general and especially hydrolyzed polyacrylonitrile.

Our concurrently filed application Ser. No. 293,661 discloses and claims solubilized polyacrylate salts of relatively strong bases. These polyacrylate salts were extremely difficult to dissolve in any reasonable time even when forming dilute solutions of less than 1% solids concentration. The use of flaked material, especially of certain thickness and particle size limits was found to produce an excellent solubilizing effect. In addition, other marked solubilizing effects were obtained by the addition of either or both of two additives, namely, polyoxyalkylene 200-4000 fatty acid esters and fine inert powders of extremely low bulk density. However, when an attempt was made to dry and flake an aqueous solution containing about 20% of polyacrylate salt the results were unsatisfactory as the polymer tended to stick to the drum drier and build up multiple layers on the drum before the doctor blade scraped or peeled off these layers. Uneven drying resulted due to the insulating effect of the inner layers of material which produced damp outer layers of the polymer. In doctoring such a substance the material was, of course, scraped off as random patches or chunks instead of the substantially continuous sheet which is obtained with materials of good flaking qualities. With an increase in molecular weight of the polymer, these unsatisfactory characteristics became progressively worse.

An object of the invention is to provide an improved method of drying polyacrylate salts of relatively strong bases.

Another object of the invention is to provide an improved process for flaking polyacrylate salts of relatively strong bases.

A further object of the invention is to provide an improved process for drying and flaking substances containing hydrolyzed polyacrylonitrile.

Other objects and advantages of the invention will be apparent to those skilled in the art especially after viewing the detailed description and examples set forth hereinbelow.

The present invention concerns the drying of an aqueous solution of a reaction product having a molecular weight above about 117,500 of relatively strong bases with polymers of certain acrylic compounds in admixture with polyoxyalkylene 200-4000 esters of a fatty acyl substance containing from 8 to 22 carbon atoms per acyl chain. The solution is deposited on a moving surface heated sufficiently to evaporate the solution to substantial dryness and the resulting substantially dried film is scraped off of the moving surface by means of a blade. A narrower aspect of the invention relates to the further incorporation of fine, inert solids of low bulk density into the mixture.

The major component of the materials dried according to the present invention comprises the reaction product of a polymer of acrylic acid, acrylonitrile, acrylamide or lower alkyl acrylates with a relatively strong base. These bases should have a dissociation constant of at least 1.8×10^{-5} at 25° C. This includes ammonium hydroxide as well as the alkaline compounds of sodium and potassium, such as the hydroxides and carbonates. The

degree of polymerization of the product is important as polyacrylate salts with molecular weights below about 117,500 are somewhat inferior for conditioning soil and have fair drum drying characteristics. Although the present process appears to be advantageous in the drying of any higher polymers of such materials, those with molecular weights above about 530,000 are currently of small interest in view of the high cost of their preparation.

While the above limits are the best approximate measurements of actual molecular weight possible at this time, it is realized that uncertainty still exists as to the accuracy of the molecular weight determination of such polymers. Accordingly, it is preferable to define the degree of polymerization of the preferred polymer, hydrolyzed polyacrylonitrile, in terms of the specific viscosity of the acrylonitrile polymer prior to the hydrolysis with the base. This value is obtained from viscosity measurements of a solution of 1 gram of the polymer made up to 100 ml. with any suitable solvent and calculation from the following equation:

$$N_{sp} = \text{Specific viscosity} = \frac{\text{viscosity of solution} - 1}{\text{viscosity of solvent}}$$

From this the molecular weight may be calculated by the Staudinger equation:

$$\text{Molecular weight} = \frac{N_{sp}}{K_m C}$$

wherein $K_m = 1.5 \times 10^{-4}$ and C = Concentration of the solution expressed as number of mols of the monomer (calculated) per liter of solution.

Specific viscosities of 2.0 and 9.0 respectively correspond to molecular weights of 70,500 and 318,000 for acrylonitrile polymers according to the best available present information. During hydrolysis or saponification in the manner set forth below it is probable that an average of about 75% of the nitrile radicals are converted into —COONa groups with much or all of the balance of the nitrile groups being converted into amido radicals. There is no reason to believe that any polymerization or polymer degradation occurs during this reaction; accordingly, the acrylonitrile polymers of 2.0 and 9.0 specific viscosities are converted into hydrolyzed polyacrylonitriles having molecular weights of about 117,500 and 530,000 respectively. These may easily be computed after assuming the conversion of 75% of the nitrile groups into —COONa radicals and 25% into —CONH₂ groups. From the above it is apparent that the molecular weight of the final polyacrylate salt is controlled by the polymerization of the acrylic monomer. However, such polymerizations and their control are well known and form no part of the present invention, therefore, they are not described herein. It will, of course, be realized that all of the polyacrylic compounds discussed herein are actually mixtures of polymers and that the stated molecular weights are averages for the mixtures.

The polyacrylate salts obtained by reacting sodium hydroxide or other relatively strong bases with polymeric acrylic acid, its lower alkyl esters and acrylamide are essentially sodium polyacrylates, etc., containing an even higher proportion of —COONa groups than hydrolyzed polyacrylonitrile. These substances are equivalents for the present purposes of hydrolyzed polyacrylonitrile of approximately the same molecular weight, however, the latter is usually preferred for soil treating compositions and the like inasmuch as it is cheaper and easier to prepare. In connection with the polyacrylic ester the expression "lower alkyl" is used herein to denote alkyl radicals containing from 1 to 4 carbon atoms, that is, methyl, ethyl, propyl and butyl esters.

In the hydrolysis or saponification of the acrylonitrile polymer or polyacrylamide the degree of hydrolysis may vary depending on the reaction conditions from about

50% up to complete hydrolysis. Hydrolysis is accomplished by mixing an aqueous slurry containing 12 or 13% of the polymer by weight with a 50% aqueous solution containing 0.8 mol of sodium hydroxide for each mol of acrylonitrile calculated as the monomer. The mixture is reacted at about 95° C. with continuous stirring. The degree of hydrolysis of the resulting product is between 75 and 85% which is within the preferred range of between 65 and 85% hydrolysis. The product contains a considerable quantity of free alkali and the addition of any suitable acid, such as sulfuric acid, is recommended in sufficient amount to adjust the pH of a 5% solution to between 7 and 11.

When an additive of the proper type is present in the above materials a striking improvement in doctoring qualities on a drum drier is noted. The polymer is readily removed from a drum drier by means of a doctor blade in the form of a substantially continuous sheet of material of substantially uniform thickness instead of as random patches or chunks of varying thickness. The improved doctoring is achieved by incorporating into the aqueous solution of the polyacrylate salt the esters of polyoxyalkylenes or polyglycols of between 200 and 4000 molecular weight with a fatty acyl substance containing from 8 to 22 carbon atoms per chain. The most desirable of these are the polyoxyalkylene 400-2500 esters of 8 to 22 carbon fatty acids. Within the molecular weight limit indicated the polyoxyalkylene radical may be obtained by the polymerization of ethylene glycol, di- and triethylene glycols, ethylene oxide, propylene oxide, 1,2-propylene glycol, 1,3-propylene glycol and the like. The preferred polyether esters are the well-known polyethylene glycol esters including Carbowax esters. The fatty acyl radical may be supplied by any suitable acylating substance such as a fatty acid, amide, acyl chloride, glyceride, etc. This radical may be either saturated or unsaturated and may contain hydroxyl groups. Among the suitable fatty acids are caprylic, lauric, palmitic, stearic, behenic, palmitoleic, oleic, ricinoleic, stearic acids and the like as well as mixtures of such acids. Specific examples of suitable substances include, inter alia, polyethylene glycol 400 monostearate, distearate, monooleate, dioleate, dilaurate, monoricinoleate, and mixed di- and triricinoleates; polyethylene glycol 600, monostearate, distearate, monooleate and dioleate; Carbowax 1000 dioleate; polyoxyalkylene 1500-2500 monostearate, and Carbowax 4000 dioleate. To effect appreciable benefits from this additive at least 0.5 part of the ester should be present per 100 parts of the polyacrylic compound and the preferred range is from 2 to 6 parts on the same basis. Quantities of the esters in excess of 10%, for example 15 or 20% or more of the weight of the polyacrylate salt are also contemplated but these appear to offer no advantage over compositions containing smaller quantities of the ester. The reason why these additives impart such excellent parting characteristics to the polyacrylate salts is not understood at present.

When fine, light, inert solids of the proper physical characteristics are added to solutions of the polymer containing polyglycol esters it serves to increase the thickness of the cake on a drum drier and thereby increase the production of the drier entirely out of proportion to the quantity of additive involved. As indicated in connection with our copending application Serial No. 293,661, which contains numerous examples of the materials under discussion, these powdered solids also facilitate dissolving the product. This material is an inert solid, that is, it does not react with either the polyacrylate salt, the ester or the water; in addition, it must have a compacted dry bulk density lower than about 30 pounds per cubic foot, in fact the preferred materials are lighter than 25 pounds per cubic foot. A suitable method for determining the compacted dry bulk density, which is also known as the tapped bulk density and settled density, is to loosely fill a 200 ml. glass graduate of about 1 1/2" internal diameter to its top mark with the dry powdered material, and repeatedly strike the bottom of the graduate sharply on a wooden table from a height of about 1'. This is continued until the upper level of the powder reaches a constant level, then a reading of the compacted or settled volume of the sample is taken and the tared graduate is weighed to determine the weight of the powdered sample. The tapped bulk density is easily computed from the settled volume and

weight of the sample. In combination with the extreme lightness a fine material is required, for example, the median particle size should be smaller than 12 microns. The term "median" is used in its ordinary statistical sense and "particle size" is employed herein to designate the maximum dimension of a particle. All suitable materials appear to be of a nontacky nature and to possess high sorptive power. Among the broad variety of such materials are the salt water and fresh water diatomaceous earths, various hydrous silicas and silicates, gypsum, phosphate rock, talcs, pyrophyllites, attapulgites, etc. of extreme fineness. While a reasonably small percentage of coarse particles will not cause any substantial decrease in the effects derived from this powder it is desirable to use materials sufficiently fine so that less than 10% by weight remains on a 200-mesh screen. Based on 100 parts by weight of the polyacrylate salt, at least 2 parts of the fine, light solids are needed for an appreciable effect and more than 20 parts produces a slurry which is too thick for ready drying and also for certain uses. In general, it may be said that 5 to 15 parts of the powder per 100 parts of the polyacrylic compound are preferred. If desired, as in the preparation of the soil conditioner for dry application described and claimed in our concurrently filed application Serial No. 293,662, additional quantities of light, fine, sorptive powders as well as dense flow-promoting solids and other like additives may be blended in any quantity into the above product subsequent to its removal from the drum drier. In making this product, the dried sheet is broken up and ground to the selected fineness in conventional equipment since flaking of the polymeric material apparently provides no advantages in this form of soil conditioner.

In producing solubilized flakes containing mixtures of the polyacrylate salt and the ester with or without the fine, inert, light powder, no special equipment is required. Conventional drum driers are heated by steam or other suitable means sufficiently in conjunction with the drum speed to evaporate the solution or slurry to substantial dryness. By this time the substantially dried film, containing less than about 5% moisture, reaches the doctor blade and is scraped off of the moving surface as a sheet. The sheet material is broken up and sized in conventional equipment such as hammer mills and vibratory screening apparatus. To dissolve readily in water, the flakes should have a thickness ranging from about 75 up to about 600 microns, the optimum range being 150 to 400 microns. In addition, substantially all, that is at least 90% by weight of the flakes, should be fine enough to pass through a 4-mesh screen and it is desirable that all of the flakes be finer than 8-mesh. Although the flaked material may contain a substantial amount of powdered fines, this is not especially desirable for materials intended to be quickly soluble. In general, not more than about 30% by weight should be finer than 100-mesh, and it is recommended that at least 80% of the material be coarse enough to remain on an 80-mesh screen.

The products of the present process are not only useful as soil conditioners in aggregating soil but also as drilling mud additives and for stabilizing soil in conjunction with calcium acrylate and other soil stabilizing agents for forming tough or rubbery soil mats suitable for highways, airplane runways, earth dams and many specialized military purposes.

A better understanding of the invention will be obtained from the following examples which illustrate the invention and are not to be construed in a limiting sense. Substantially the same materials were used as constituents of the feed in varying quantities to obtain the best comparison of the effects of the additives. The only difference was in the use of hydrolyzed polyacrylonitrile of different degrees of polymerization as some of the runs were made with the polymer derived from polyacrylonitrile having a specific viscosity of about 2.8 (165,000 mol. wt., Staudinger) while others were obtained from acrylonitrile polymers of 4.1 specific viscosity (241,000 mol. wt., Staudinger). The same Laboratory model double drum drier manufactured by Blaw Knox Inc. and equipped with chromium plated cast iron 6" diameter drums 8" long was used for all runs under comparable operating conditions.

Example.....	A	I	II	III	IV	B	C	V	VI	VII
Feed Composition:										
Polymer, lbs.....	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Celite HSC, lbs. ¹	0	1.0	1.0	1.0	1.0	0	0	0	0.5	1.0
Carbowax 1,000 dioleate, lbs. ¹	0	0.3	0.3	0.3	0.3	0	0	0.3	0.3	0.3
Total solids, wt. percent.....	22.0	22.0	22.0	22.0	22.0	22.0	22.0	20.5	21.3	22.0
Polymer, Mol. Wt., Staudinger.....	165,000	165,000	165,000	165,000	165,000	241,000	241,000	241,000	241,000	241,000
Temperature.....	Room	Room	Room	Room	Room	Room	Room	Room	Room	Room
Drum:										
Steam press., p. s. i. g.....	60	58	70	70	68	60	70	68	68	68
Speed, R. P. M.....	3.3	3.3	5.0	5.0	5.0	3.3	5.0	5.0	5.0	5.0
Clearance, Mils.....			1-2	1-2	1-2	4-6	4-6	10	4-10	4-10
Product:										
Sheeting characteristics.....	Poor	Excellent	Excellent	Excellent	Excellent	Poor	Poor	Good	Good	Good
Discharge rate, lbs./hr./sq. ft.....		1.60	1.78	1.55	1.85	0.52		0.88	1.07	1.46

¹ A registered trade-mark of the Johns-Manville Corp. for a product composed of a diatomaceous earth fluxed with soda ash and then calcined. A typical analysis shows: SiO₂—90.9%, Al₂O₃—3.7, Na₂O—2.5%. This material has an average particle size of from 7 to 9 microns (Oden method) with a median particle size below 10 microns. Less than 7% by weight remains on a 150-mesh screen and the compacted bulk density is between 14 and 17 pounds per cubic foot.

² Mixed polyethylene glycols having an average molecular weight of approximately 1,000 diesterified with oleic acid.

In reviewing the results of the above examples, it is apparent that the unsatisfactory sheeting characteristics of the polyacrylic compound became either good or excellent in every instance in which the polyoxyalkylene ester was present either alone or with the light, fine inert powdered solids. In addition, a comparison of Examples V, VI and VII discloses that a substantial improvement in the production rate is brought about by incorporation of the light, fine solids and that this improvement is more than proportional to the amount incorporated with the hydrolyzed polyacrylonitrile.

It will, of course, be understood that the present invention contemplates not only the various materials mentioned above but also any other substances which are compatible therewith. Thus fertilizers, weed killers, insecticides and other materials used in treating soil may be combined with the materials disclosed herein as desired to perform their usual functions.

Having described our invention what we claim as new and desire to secure by Letters Patent is:

1. A process which comprises mixing an aqueous dispersion of a reaction product having a molecular weight above about 117,500 of a monovalent base with a dissociation constant no smaller than 1.8×10^{-5} and a polymer of a compound of the group consisting of acrylic acid, acrylonitrile, acrylamide and lower alkyl acrylates, at least about 0.5 part of an ester of a polyoxyalkylene compound having a molecular weight between 200 and 4,000 and a fatty acid containing from 8 to 22 carbon atoms per acyl chain, and between 2 and 20 parts of an inert nontacky solid of high sorptive power having a compacted dry bulk density less than 30 pounds per cubic foot and a median particle size smaller than 12 microns; depositing the dispersion on a moving surface heated sufficiently to evaporate the solution to substantial dryness, and scraping the resulting substantially dried film off of the moving surface with a blade.

2. A process which comprises mixing an aqueous dispersion of 100 parts by weight of hydrolyzed polyacrylo-

nitrile obtained by hydrolyzing polyacrylonitrile having a specific viscosity above about 2.0 with a monovalent base having a dissociation constant no smaller than 1.8×10^{-5} , at least about 0.5 part of an ester of a polyoxyalkylene compound having a molecular weight between 200 and 4,000 and a fatty acid containing from 8 to 22 carbon atoms per acyl chain, and between 2 and 20 parts of an inert nontacky solid of high sorptive power having a compacted dry bulk density less than 30 pounds per cubic foot and a median particle size smaller than 12 microns; depositing the dispersion on a moving surface heated sufficiently to evaporate the solution to substantial dryness, and scraping the resulting substantially dried film off of the moving surface with a blade.

3. A process which comprises mixing an aqueous dispersion of 100 parts by weight of hydrolyzed polyacrylonitrile obtained by hydrolyzing polyacrylonitrile having a specific viscosity above about 2.0 with a monovalent base having a dissociation constant no smaller than 1.8×10^{-5} , between 2 and 6 parts of an ester of a polyoxyalkylene compound having a molecular weight between 400 and 2,500 and a fatty acid containing from 8 to 22 carbon atoms per acyl chain, and between 5 and 15 parts of an inert nontacky solid of high sorptive power having a compacted dry bulk density less than 25 pounds per cubic foot and a median particle size smaller than 12 microns; depositing the dispersion on a moving surface heated sufficiently to evaporate the solution to substantial dryness, and scraping the resulting substantially dried film off of the moving surface with a blade.

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