Cl. 260

Published Apr. 20, 1943

Serial No. 404,237

ALIEN PROPERTY CUSTODIAN

DRY POLYMERIZATION PRODUCTS

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No Drawing. Application filed July 26, 1941

The present invention relates to substantially dry compositions of matter containing synthetic polymerization products; more specifically it relates to compositions which show the remarkable property of being easily and completely distributable to form stable aqueous dispersions when agitated with water or aqueous media. The preferred embodiment of the invention are dry preparations of polyvinyl compounds, more particularly polymerization products of compounds having the group

$$\diagdown C{=}CH_2$$

and interpolymerization products of said compounds.

Synthetic polymerization products, especially polyvinyl compounds, are widely applied in the form of aqueous dispersions; this mode of application has the advantage that the polymerization products may be used in the liquid phase and that, thereby, the numerous drawbacks involved in the use of organic solvents are avoided.

It has, however, in practically all cases proved to be very difficult for the consumers of hitherto known polymerization products to prepare aqueous dispersions thereof, since the dispersing of said products requires knowledge and apparatus commonly not available to the majority of the industries consuming and applying plastics.

The manufacturers of synthetic polymerization products, therefore, proceeded to prepare and to market aqueous dispersions of said products even though the transportation of the large amounts of water proved to be very uneconomical, quite apart from the fact that sometimes the aqueous dispersions coagulate during transportation or storing, thus causing further inconvenience.

Now, it has been found that it is possible to obtain, by drying aqueous dispersions of polymerization products, powders of such a form that they may again be emulsified in water with formation of dispersions having the same properties as the dispersions originally used. To this end, dispersions of such polymerization products are used as are prepared by means of water-soluble high-molecular protective colloids. As products suitable for the purpose of the present invention there are mentioned: polyvinyl alcohol and the water-soluble derivatives thereof, such as, products partially esterified with formic acid, acetic acid, propionic acid or butyric acid, products partially acetalized with formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde or cyclohexanone, in which cases, however, only such a number of ester-, aldehyde-, or keto-groups may be present that the products are still water-soluble; furthermore, polyethylene oxide, salts of polyacrylic acid or of polymethacrylic acid, for instance, the ammonium, potassium or sodium salts of these acids; or the salts of interpolymerization products from maleic acid or crotonic acid and vinyl compounds as well as the water-soluble amides of polyacrylic and polymethacrylic acid. Such dispersions are described in USA patent No. 2227163.

As polymerization products which may be worked up to form dry preparations there may be mentioned, for instance: polymerization and interpolymerization products of vinylacetate, vinylformate, vinylpropionate, vinylbutyrate, vinylbenzoate; furthermore, vinylchloride; acrylic acid- and methacrylic acid methylester, acrylic acid- and methacrylic acid ethylester, acrylic- and methacrylic acid propylester; vinylmethylketone, styrene, vinylether as well as vinylbutylether.

It is advisable to effect the drying under conditions as mild as possible so that the emulsifying property of the water-soluble emulsifier is not affected thereby. Therefore, the drying is performed advantageously at a temperature as low as possible, if necessary, under reduced pressure. In order to prevent the moist or dry particles of the polymerization products to adhere to each other, the temperature is not allowed to rise up to the point at which the particles begin to sinter or even to melt. Furthermore, it is advisable to adjust the dispersions to a neutral pH-value prior to the drying. As drying processes there may be applied, besides the known processes carried out under reduced pressure, spray-dryings, for instance, according to the "Krause" or "Nubilosa" systems. Such drying processes are, for instance, described in "Chemische Apparatur," vol. 28, No. 4, pages 49–52. Furthermore, it is also possible to freeze the aqueous dispersions and, thereupon, to dry them with application of reduced pressure and of drying agents, for instance, concentrated sulfuric acid or calcium chloride.

It could not be foreseen that it would be possible to dry aqueous dispersions of hydrophobic or thermoplastic masses with formation of powders yielding again, when agitated with water, stable finely disperse latices of original quality especially in view of the fact that the emulsifiers used are present only in small quantities of, for instance, 2–3% calculated upon the polymer. The effect is all the more surprising because coagulates which are often formed in the prep-

aration of such dispersions cannot be converted by means of water into the desired highly disperse state.

The use of polymerization products in the form of their aqueous dispersions has recently found a wide field of application. For instance, coated or finished fabrics, synthetic leather-like products prepared from leather- or textile fibers as well as coating agents are prepared to a large extent by means of such synthetic latices. In all these cases it is of great technical advantage that one may start from solid, particularly from pulverized, products since, as above stated, it is thereby possible to reduce the costs of freight and packing when the goods are transported; furthermore, losses due to the formation of skins and crusts are avoided and the consumer is in the position to adjust the synthetic latex to any desired concentration directly before use. The latices in question are prepared by introducing the dry powders into the desired quantity of water while agitating, for instance, while well stirring. The usual auxiliary agents such as softeners, pigments or filling agents may then be added as desired, while stirring.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

(1) A highly viscous 50% dispersion of polyvinylacetate prepared according to one of the usual methods by polymerization of vinylacetate with the same quantity of a 5% aqueous solution of polyvinyl alcohol and consisting of particles of 0.5–2μ, is poured on drying sheets to form layers of 2–3 cm thickness which are frozen at —10° C. In this form the sheets are placed in a drying-oven in which a pressure of 0.1 mm is maintained by means of an efficient pump. A vessel containing concentrated sulfuric acid serves as receiver. The aggregate is kept at room temperature for 24 hours. In this way a product is obtained which is practically free from water and may easily be pulverized by means of a comminuting apparatus. When the powder thus obtained is introduced into water, while stirring, a highly-viscous dispersion like that originally used is obtained.

(2) The dispersion used in example 1 is diluted with water to a dry contents of 40% and adjusted to a pH-value of 7. In a "Nubilosa" drying apparatus the dispersion is atomized by means of air of +12° C, care being taken that the inferior part of the tunnel drier is kept at low temperature by external cooling.

A powder fine as flour is obtained which, when stirred with water, again yields a stable latex. Into the latter the desired quantity of softener may be introduced, by stirring quickly. The emulsion obtained is suitable for preparing coated or finished fabrics or the like.

Instead of the "Nubilosa" apparatus there may be used with the same success a "Krause" drier; in the latter case, the temperature of the air advantageously amounts to 40° C–50° C.

(3) Into a 45% dispersion prepared by means of an interpolymerization product from 70 parts by weight of vinylacetate and 30 parts by weight of vinylchloride and an aqueous 3% solution of sodium polyacrylate, there are introduced 2% of ammonium carbonate, calculated upon the dry substance. The dispersion is then atomized by means of a "Nubilosa" or a "Krause" drier as described in example 2. By means of water the fine powder obtained may be re-transformed into a finely dispersed latex which is ready for use.

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