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AQUEOUS POLYETHYLENE DISPERSIONS PRODUCED BY SUBJECTING MOLTEN POLYMER IN WATER TO A HIGH RATE OF SHEAR

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Several methods have been described for the manufacture of dispersions of polythene referred to hereinafter as normally solid polyethylene. They include aqueous polymerisation to give polymers directly as an emulsion; dissolving the material in a solvent, emulsifying the solution with water, and removing the solvent; and milling the solid material with dispersing agents or protective colloids, and adding water. These methods rarely give good quality stable dispersions, and are often expensive.

We have found that although normally solid polyethylene does not produce a free-flowing liquid when melted, and has a high viscosity, yet we can emulsify molten polythene with water in a colloid mill or similar device.

According to the present invention, we manufacture dispersions of normally solid polyethylene by a process which comprises passing molten normally solid polyethylene with water, at a temperature above 115° C. and at sufficient pressure to keep the water in the liquid state, through an emulsifying device, and then releasing the pressure.

Convenient emulsifying devices are any machines which provide high rates of shear and keep a substantial pressure on the materials before emulsification, particularly a suitably designed colloid mill or homogenizer with a pressure casing. The rate of shear is one of the factors which determines the particle size of the dispersed normally solid polyethylene, but a suitable rate is provided by either of these types of emulsifying device. Colloid mills have two surfaces situated within about one-hundredth of a centimetre moving at high speed relative to each other, and the rate of shear is determined by the speed and the gap. They can be adapted so that the mixture is under pressure. Suitable conditions for a 10 centimetre diameter mill, for example, are that the gap shall be between 5 and 10 thousandths of a centimetre, and the rotor shall rotate at between 5000 and 15,000 revolutions per minute. When working in a homogenizer we pump hot liquid water under pressure, with molten polythene, through a narrow opening between a valve and its seat; the rate of shear is determined by the rate of flow and the size of gap. Both machines are modified so that the water feed and the polythene feed are hot and above two atmospheres pressure.

The temperature of operation must be above 115° C., which is the melting point of normally solid polyethylene, and as normally solid polyethylene does not produce a free-flowing liquid

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when melted, it is preferably at least 130° C. The top temperature is limited both by the critical temperature above which water cannot be a liquid and by the decomposition of normally solid polyethylene, and preferably does not exceed 250° C.; when emulsifying agents are present it is limited by the temperature at which they become inactive, which is generally about 160° C. The minimum pressure needed exceeds the vapour pressure of water at the operating temperature, and is therefore at least 2 atmospheres absolute and generally at least 3–6 atmospheres. For convenience, however, we prefer to use rather high pressures between 20 and 50 atmospheres.

The amount of water used is between 1 and 5 parts by weight per part of normally solid polyethylene, preferably between 2 and 5 parts by weight per part of normally solid polyethylene. It is not commercially attractive to make dispersions which contain as little as 15% of normally solid polyethylene, and technical difficulties arise in making dispersions containing as much as 35% of solid ethylene polymers. We also prefer to add an emulsifying agent in order to assist in preparing the dispersion and to increase its stability. Agents which are not decomposed at the emulsification temperature are effective, and of these we prefer the fatty acid compounds known broadly as soaps, for example the potassium and sodium salts of stearic, palmitic, and other long chain carboxylic acids, as well as compounds of these acids with other bases such as triethanolamine. They are most advantageously introduced by incorporating the carboxylic acid in the normally solid polyethylene and dissolving the basic compound in the water, so that during emulsification the agent is formed in situ. The amount of agent required is usually between 1 and 20 parts by weight per 100 parts of normally solid polyethylene, the optimum result being obtained with between 5 and 15 parts.

The water and normally solid polyethylene can be heated separately and pumped in under pressure, or mixed before pumping in, or by any other convenient means. For industrial operation it is desirable to operate continuously, and in order to get accurate control we prefer to feed in the melted normally solid polyethylene through a heated screw extrusion pump and a gear pump, and the water through a measuring pump which raises its pressure sufficiently. We also prefer to pass these feeds through heated tubes to get the temperature high enough before entering the emulsifying device.

It is very desirable to cool the dispersion within about 10 seconds of leaving the emulsifying device, in order to avoid coalescence of the particles. This is done by making the connecting space between the blow-off valve where the pressure is released and the outlet of the emulsifying device as small as possible. The releasing of the pressure can be done into the air so as to allow steam to flash off and thus cool the emulsion to 100° C., but we prefer to cool further than this by blowing off the dispersion direct into some cooled dispersion at 30–60° C.

The normally solid polythene particles in the dispersions obtained by this process can readily be made as small as 5–20 microns.

The invention is illustrated by the following example.

Example

A colloid mill with a gap of .01 cm. and a 10 cm. diameter rotor in a steel casing to withstand pressures up to 100 atm. was fitted with a pressure release valve for delivering the dispersion, a pressure tight gland for the drive, and a steam jacket. It was also fitted with two feed pipes, one of which led from a water heater fed by a pump from a stock tank while the other led from a heater for the normally solid polyethylene fed by a screw extrusion pump. 300 kgm. of water with 6.6 kgm. of triethanolamine were mixed in the stock tank. 100 kgm. of normally solid polythene ("Alkathene" brand of polythene, Grade 70, "Alkathene" being a registered trade-mark) were mixed with 10 kgm. of stearic acid on steam-heated rubber milling rolls and fed into the hopper of the screw extrusion pump. The aqueous phase was fed into the mill at a rate of 20 kgm./hr. and the pressure release valve adjusted to maintain a pressure of 40 atm. in the mill. The steam was then turned on to the steam jacket of the mill, and the electric heaters for the water and the normally solid polythene switched on. When the water, normally solid polyethylene and mill temperatures had reached 150° C. the mill was started and run at 7500 R. P. M. and the screw extrusion pump started so as to feed the normally solid polythene mixture at a rate of 10 kgm./hr. The exit from the pressure release valve was at the bottom of an open 1-litre tank fitted with an overflow delivering into a receiver. 2 litres of aqueous phase at 35° C. were circulated through this tank and through a cooler. The dispersion emerged from the release valve, mixed with and gradually displaced the aqueous phase in the cooling system, so that after 15 mins. a dispersion containing 30% normally solid polyethylene was being collected from the overflow. The average particle size of the dispersed normally solid polyethylene was 10 microns

Dispersions made according to the process of this invention are of most value in coating paper in order to waterproof it, and in impregnating fabrics to stiffen them. The normally solid polythene retains its well known toughness, which is such an important factor in its use for coating and impregnating materials.

What I claim is:

1. A process for the manufacture of polyethylene dispersions which comprise subjecting a mixture of molten, normally solid polyethylene and one to five parts by weight of water per part of polyethylene at a temperature above 115° C. and at a sufficient pressure to keep the water in the liquid state, to a high rate of shear such that the dispersed particles of said polyethylene have an average particle size of from about 5 to 20 microns, and then releasing the pressure.

2. A process as claimed in claim 1 carried out at a temperature between 130° and 250° C. and at a pressure between 20 and 50 atmospheres.

3. A process as claimed in claim 1 wherein between 2 and 5 parts by weight of water are used per part of normally solid polyethylene.

4. A process as claimed in claim 1 carried out in the presence of an emulsifying agent.

5. A process as claimed in claim 1 carried out in the presence of a soap as an emulsifying agent, the soap being made in situ by having a higher fatty acid dissolved in the normally solid polyethylene and a base dissolved in the aqueous phase.

6. A process as claimed in claim 1 in which an emulsifying agent is employed and in which the amount of emulsifying agent is between 1 and 10 parts by weight per 100 parts of normally solid polyethylene.

7. A process as claimed in claim 1 carried out in the presence of an emulsifying agent and at a temperature between 130° and 160° C.

8. A process as claimed in claim 1 in which the emulsion is rapidly cooled immediately after the pressure has been released.

9. A process as claimed in claim 1 in which the pressure is released within 10 seconds after the dispersion has been subjected to a high rate of shear.

10. A process for the continuous manufacture of polyethylene dispersions which comprises continuously and simultaneously introducing molten, normally solid polyethylene and one to five parts by weight of water per part of said polyethylene to a colloid mill, and subjecting the mixture so formed at a temperature above 115° C. and at a sufficient pressure to keep the water in the liquid state, to a high rate of shear such that the dispersed particles of said polyethylene have an average particle size of from about 5 to 20 microns and then releasing the pressure.

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