

Description

BACKGROUND OF THE INVENTION

5 Many polymerizable monomeric materials, and particularly vinyl chloride, are being polymerized today on a large scale commercially either in suspension media or in aqueous dispersion or emulsion, i.e., latex form, employing various colloidal suspension agents, emulsifiers or soaps, or synthetic detergent type dispersing agents. In these methods of polymerization, and particularly in suspension polymerization, vigorous agitation is depended upon to suspend and disperse the monomer particles or droplets throughout
 10 the reaction media and to maintain such suspension or dispersion during the polymerization reaction and to assist in heat transfer to the reactor cooling surfaces. However, in most instances, polymer particles produced in accordance with these processes are not spherical in shape. Small particles tend to agglomerate into irregular shaped particles. These irregular shaped particles result in a resin with a low bulk density. High bulk density is a desirable polymer property because it gives faster extrusion rates, easier
 15 handling and shipping advantages.

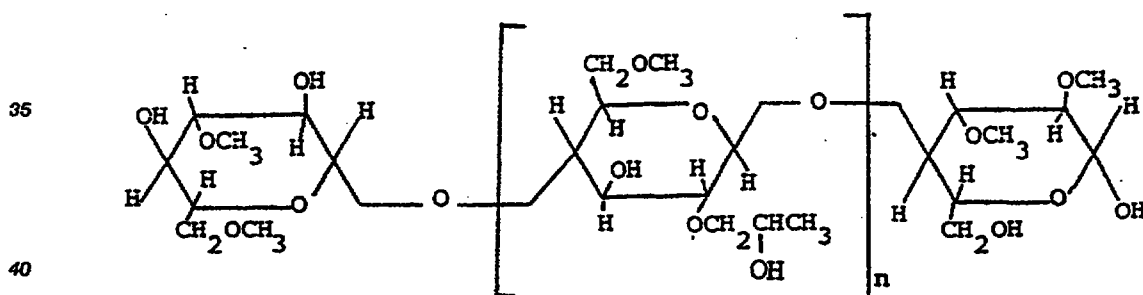
Heretofore it has been suggested to use an excess of soap in the reaction medium to overcome agglomeration. This does prevent agglomeration, however, the polymer particles are very small and spherical in shape. Small particles have other processing disadvantages.

An excess of soap would result in the micro-suspension or emulsion process which give small particle resin, which is used in different end use applications than a resin made by this invention, which is a
 20 suspension process. An example of this type of process is disclosed in U.S. Patent 4,319,012,

It is desirable to produce a polymer having large particle size and the particles be spherical in shape thus giving a high bulk density resin.

25 SUMMARY OF THE INVENTION

It has unexpectedly been found that high bulk density vinyl resins, having substantially spherical particles can be prepared by the suspension polymerization process by employing as a dispersant a non-ionic, high molecular weight alkyl hydroxy cellulose polymer, preferred is a hydroxypropyl methyl cellulose
 30 polymer having the formula:



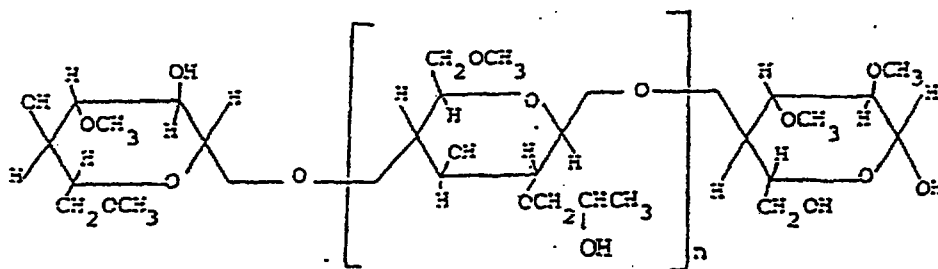
where n is from 300 to 1500.

Suitable polymer dispersants have a molecular weight of from 50,000 to 500,000. The dispersant should
 45 also have a viscosity range of from 1 to 100 Pa.s as measured as 2% in water at 20° C according to ASTM D 2363.

DETAILED DESCRIPTION

50 While the present invention is specifically illustrated hereinafter with regard to the suspension polymerization of vinyl chloride, it is to be understood that this is merely for purposes of illustration and convenience since the present process may likewise be employed in the suspension polymerization of any polymerizable ethylenically unsaturated monomer or monomers.

In detail the present invention refers to a process for producing spherical particles of polyvinyl chloride resin in the presence of a dispersant, characterized in that said dispersant is a hydroxypropyl methyl
 55 cellulose polymer having the formula:



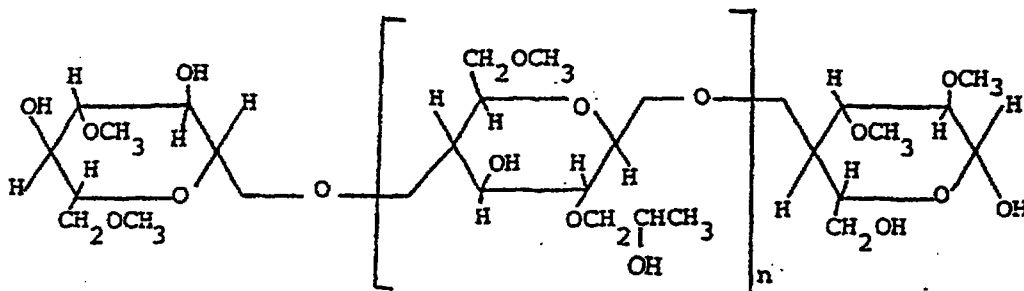
wherein n is from 300 to 1500, said dispersant has a molecular weight of from 50,000 to 500,000, a viscosity of from 1 to 100 Pa.s as a 2% solution in water at 20°C as measured by ASTM D 2363, said dispersant is employed in the range of from 0.02 to 0.1 part by weight said part by weight based on 100 parts by weight of polymerizable monomer, wherein said polyvinyl chloride resin has a bulk density greater than 0.58 g/cm³ and a Dop porosity greater than 0.06 cm³/g.

The monomers which may be employed in the present invention include vinyl chloride and polymerizable olefinic monomers copolymerizable therewith having at least one terminal $\text{CH}_2=\text{C}<$ grouping such as the other vinyl halides and vinylidene halides, for example, vinyl bromide, vinylidene chloride; acrylic acid; esters of acrylic acid, such as methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, cyanoethyl acrylate; methacrylic acid; esters of methacrylic acid, such as methyl methacrylate, butyl methacrylate, nitriles, such as acrylonitrile, methacrylonitrile; acrylamides, such as methyl acrylamide, N-methylol acrylamide, N-butoxy methacrylamide; vinyl ethers, such as ethyl vinyl ether, chloroethyl vinyl ether; the vinyl ketones, such as methyl vinyl ketone; vinyl naphthalene; allyl and vinyl chloroacetate; vinyl acetate; vinyl pyridine; and mixtures of any of these types of monomers and other olefinic monomers copolymerizable therewith including esters of maleic and fumaric acid; and other copolymerizable olefinic monomers of the types known to those skilled in the art.

The present invention is particularly applicable to the polymerization of vinyl chloride, either alone, or in admixture with one or more other polymerizable olefinic monomers having at least one terminal $\text{CH}_2=\text{C}<$ grouping in amounts up to 50% preferably up to 20%, weight of comonomer, based on the weight of the monomer mixture.

The most important and salient feature of the present invention is the colloidal stabilization, or dispersant system, that is employed in the polymerization reaction for the purpose of stabilizing the dispersed monomer droplets against coalescence. It has quite unexpectedly been found that spherical polymer particles having high bulk density can be prepared when using as a component of the dispersant system at least one dispersant that is a non-ionic high molecular weight alkyl hydroxy cellulose polymer. Preferred is a hydroxypropyl methyl cellulose polymer. Suitable polymers have a molecular weight of from 50,000 to 500,000, preferably from 75,000 to 150,000, with a chain length of from 300 to 1500 repeating units, preferably from 400 to 700. The polymer should also have a viscosity range of from 1 to 100 Pa.s, preferably from 2 to 10 Pa.s, as measured by a 2% solution in water at 20°C according to ASTM D 2363. Polymers such as these are normally identified by their viscosity rather than molecular weight. Viscosity is the important characteristic for operation in this invention. Wherever viscosity is expressed in this specification it is arrived at by measuring as a 2% solution in water at 20°C according to ASTM D 2363.

A suitable non-ionic, high molecular weight polymer for use as a dispersant in this invention is hydroxypropyl methyl cellulose having the following formula:



where n is from 300 to 1500.

The chain length of the dispersant is very important for this invention. If the chain length is longer than

the recommended length, then the aqueous medium cannot be properly agitated during polymerization because the aqueous medium (water) is thickened excessively. If the chain length is shorter than the recommended length, then the droplets of suspended vinyl monomer have a tendency to agglomerate, thereby reducing bulk density.

5 Dispersants of this invention may be readily obtained from the Dow Chemical Company. They are sold under the trade name of Methocel. Lower viscosity materials are also sold under the same trade name but they do not work to make spherical shape, high bulk density resins.

The level of non-ionic, high molecular weight polymer dispersant used in this invention is in the range of 0.01 to 1.0, preferably 0.02 to 0.10, part by weight per 100 parts by weight of polymerizable monomer to
10 give satisfactory results. Different viscosity hydroxypropyl methyl cellulose dispersants within this invention (1 to 100 Pa.s) will require different levels to get optimum results. For example, higher viscosities such as 75 Pa.s will require slightly higher levels than a 4 Pa.s material. Optimizing the recipe is well within the skill of those in the art. More than one hydroxypropyl methyl cellulose dispersant may be used in combination.

In the process of this invention other surfactants may be employed, along with the high molecular
15 weight hydroxypropyl methyl cellulose dispersant. Among the surfactants that are satisfactory, include the water-soluble, polyether containing nonionic surfactants. Examples of polyether containing nonionic surfactants useful are those falling within the following generic classes: (1) polyoxyethylene alkylphenols; (2) polyoxyethylene alcohols; (3) polyoxyethylene esters of fatty acids; (4) polyoxyethylene alkylamines; and (5) polyoxyethylene alkylamides. As examples of surfactants in the above-named classes there may be named
20 the following: polyoxyethylene (20) sorbitan monooleate, polyoxyethylene (20) sorbitan monolaurate, polyoxyethylene (20) sorbitan monopalmitate, polyoxyethylene (20) sorbitan monostearate, polyoxyethylene (40) stearate, polyoxyethylene (50) stearate, polyoxyethylene esters of mixed fatty and resin acids, polyoxyethylene (20) palmitate, polyethylene glycol monolaurate, polyethylene glycol monooleate, polyethylene glycol ricinoleate, polyethylene glycol monostearate, polyethylene glycol distearate, polyoxyethylene (25)
25 stearate, polyoxyethylene (40) stearate, polyoxyethylene (25) castor oil, polyoxyethylene (52) castor oil, polyoxyethylene (9) laurate, polyoxyethylene (15) tallate, polyoxyethylene (9) lauryl ether, polyoxyethylene (12) lauryl ether, polyoxyethylene (23) lauryl ether, polyoxyethylene (6) tridecyl ether, polyoxyethylene (10) tridecyl ether, polyoxyethylene (10) oleyl ether, polyoxyethylene (20) oleyl ether, polyoxyethylene (50) oleyl ether, polyoxyethylene (15) cetyl stearyl ether, polyoxyethylene (20) stearyl ether, polyoxyethylene (30)
30 stearyl ether, polyoxyethylene (8) tridecyl ether, polyoxyethylene (9) nonyl phenyl ether, polyoxyethylene (21) coconut ester. The above compounds have a multiplicity of functional groups and accordingly a very large number of modifications is possible. Mixtures of said compounds can also be used.

Non-polyethylene oxide containing surfactants as taught in U.S. Patent 4,435,524, may be used together with a polyethylene oxide containing surfactant and the high molecular weight hydroxypropyl
35 methyl cellulose dispersant. Suitable non-polyethylene oxide containing surfactants are those compounds from the sorbitan ester family or the glycerol ester or polyglycerol ester families, as well as the polyvinyl alcohols, which do not contain polyethylene oxide segments. As examples of such surfactants there may be named sorbitan trioleate, sorbitan tri-stearate, sorbitan monooleate, sorbitan monopalmitate, glycerol monooleate, glycerol monostearate, triglycerol monooleate, 72.5% hydrolyzed polyvinyl acetate.

40 The polyethylene-oxide containing surfactant may be used at a level of from 0.005 parts by weight to 1.0 parts by weight per 100 parts by weight of monomer. Preferably, an amount of 0.0075 parts by weight to 0.5 parts by weight per 100 parts by weight of monomer is used. The non-polyethylene oxide containing surfactant may be used at a level of from 0.005 parts by weight to 0.2 parts by weight per 100 parts by weight of monomer, preferably from 0.02 parts by weight to 0.1 parts by weight per 100 parts by weight of
45 monomer.

Furthermore, sodium laurylsulfonate may be used.

Any of the well known dispersants operative in aqueous media may be employed. These include among others, methyl cellulose, low molecular weight hydroxypropyl methyl cellulose, polyvinyl alcohol, lauryl alcohol, sorbitan monolaurate polyoxyethylene, nonylphenoxy polyoxyethylene ethanol, hydrolyzed
50 polyvinyl acetates.

In the suspension process, the monomer droplet is formed and is coated or surrounded by the dispersant. The individual monomer droplets are maintained in the suspension and do not agglomerate. The coating of dispersant becomes a part of the outside surface of the particles in the finished state. An analysis of the resin particle surface may be made by ESCA techniques to show that the dispersant is on the
55 surface of the polymerized resin particle.

Among the catalysts or initiators that may be employed in the present invention are the free radical yielding catalysts or initiators, such as the alkanoyl, aroyl, alkaroyl and aralkanoyl diperoxides and monohydroperoxides, azo compounds, peroxyesters, percarbonates. As examples of such catalysts, there

may be named benzoyl diperoxide, lauryl diperoxide, diacetyl peroxide, cumene hydroperoxides, methyl ethyl ketone peroxide, diisopropylbenzene hydroperoxide, 2,4-dichlorobenzoyl peroxide, benzoyl peroxide, naphthoyl peroxide, lauroyl peroxide, acetyl cyclohexane sulfonyl peroxide, t-butyl perbenzoate, di-t-butyl perphthalate, diisopropyl peroxydicarbonate, 2-ethyl hexyl peroxydicarbonate, di (sec-butyl) peroxydicarbonate azo-bisisobutyronitrile, α,α' -azodiisobutyrate. The choice of any particular free radical yielding catalyst is dictated in part by the particular monomer or monomers to be polymerized and by the color requirements of the polymer or copolymer to be produced. Further, more than one catalyst may be employed in the polymerization recipe. Usually the amount of catalyst or catalysts employed will be in the range of 0.005% to 1.0% by weight, based on the weight of the monomer or monomers being polymerized.

10 Preferably, the amount of catalyst(s) will be in the range of 0.02% to 0.10% by weight.

In aqueous suspension polymerization the reaction is usually conducted at a temperature in the range of 0°C to 100°C depending upon the particular monomer or monomers being polymerized. It is preferred, however, to employ temperatures in the range of 40°C to 70°C, since, at these temperatures, polymers having the most all around beneficial properties are produced. This is particularly so in the case of making

15 homopolymers and copolymers of vinyl chloride. The time of the reaction will vary from 2 to 15 hours.

The suspension polymerization process may be carried out at autogenous pressures although superatmospheric pressures of up to 10 atmospheres or more may be employed with some advantage with the more volatile monomers.

In the suspension polymerization procedure, the various ingredients are thoroughly mixed prior to the start of the reaction. That is, the aqueous medium, preferably distilled water, the monomer to be polymerized, such as vinyl chloride, the non-ionic, high molecular weight polymer dispersant, other optional dispersants or surfactant, and an oil-soluble catalyst are all mixed together at a temperature below that at which the particular catalyst being used becomes active. While this mixing can be done in a vessel apart from the reaction vessel, for convenience and practical reasons the mixing of the ingredients is done in the

20 polymerization reaction vessel under an inert atmosphere, particularly where the monomer or monomers being employed are subject to oxidation.

In the suspension polymerization process of this invention, agitation or stirring of the reaction medium is necessary during the entire polymerization reaction period, that is, from 0% conversion to completion of the reaction. Prior to the start of the polymerization reaction, the polymerization mixture is agitated to provide

25 shear action to disperse or suspend the monomer(s) in the reaction medium in the form of droplets. These droplets should be of such size that when transformed into polymer particles, which are spherical, the same will be of the desired size. The polymer particles produced in accordance with this invention should have a diameter in the range of 30 μm to 1000 μm . Preferably, for most end uses, the polymer particles will have a diameter in the range of 50 μm to 500 μm .

Various means, known to those in the art, may be employed to get and maintain the proper agitation and shearing action. The reaction vessel or polymerizer is made of stainless steel or glass lined and fitted with a heating and cooling jacket and having a rotatable shaft mounted centrally thereof. On said shaft are mounted one or more agitator blades, which may be flat or curved. Further, one or more baffles are employed which are mounted on the inner wall of the reactor or adjacent thereto. The baffles give an up and down, pumping action to the reaction medium in addition to the circular motion thereof created by the

30 agitator blades.

The amount of agitation desired or necessary to obtain the desired results will vary depending upon the particular monomer or monomers being polymerized, as well as the particular polymer particle size desired in the end product. This means that the agitation speed of the rotatable shaft carrying the agitator blades

35 must be regulated within certain limits. There are many variables involved in obtaining the optimum conditions for any particular polymerization recipe, such as, for example, the size of the reactor, the number of blades on the rotatable shaft as well as the shape thereof, which will dictate the agitation speed to be employed in obtaining the desired particle size of the polymer particles. It is to be noted that as the reactor capacity is increased or decreased, adjustment in the length, width and pitch of the blades must be made in

40 order to achieve the desired agitation and shear action. It should also be noted that the agitation and shear action will be influenced by the monomer(s) being polymerized and the temperature of the polymerization reaction. It is well known to those skilled in the art of polymerization how to make the changes in agitation to accomplish the desired affects on a particular polymerization run.

While the present invention may utilize any of the conventional suspension polymerization techniques, it is possible to utilize a full reactor technique, particularly for reducing chances of polymer buildup in the reactor. By full reactor technique is meant that the reaction vessel is completely filled with the polymerization medium at the start of the reaction and kept that way throughout the entire period of the reaction by the continuous addition thereto of additional reaction medium ingredients of which are in the same proportion as

45

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the startup. Upon the addition of a certain predetermined amount of aqueous polymerization medium, the polymerization reaction is terminated, usually by the addition thereto of a shortstopping agent or by rapid cooling. The necessity for the addition of aqueous polymerization medium is due to the shrinkage in volume of the reaction medium produced by the conversion of the monomer or monomers to the polymeric state.

5 The resin particles produced by this invention are spherical in shape. Spherical particles offer advantages over non spherical resin particles. Fast extrusion rates and low shipping costs are but two of the many advantages gained by using spherical particles.

A very good method to measure the spherical shape of resins is to determine the shape factor by optical procedures. The image of the particle is projected onto a flat surface to provide a two dimensional view. The shape factor of a particle is determined by inscribing and circumscribing the resin particles flat image with a circle. The ratio of the diameters of the inscribed circle to the circumscribed circle is the number known as the shape factor.

10 In the case of a perfect circle, the inscribed and circumscribed circles would have the same diameter and, therefore, the shape factor would be unity (1.0). The more near the shape factor is to 1.0 the more spherical the particle.

Commercial polyvinyl chloride resin particles typically have a shape factor ranging from 0.7 to 0.88. The shape factor of the resin particles of this invention is greater than 0.9, preferably greater than 0.93, and more preferably greater than 0.95.

The preferred optical procedure used to determine the shape factor is to first screen the particles through a 105 μm screen and run the test on the particles larger than 105 μm . Static interference can also affect this optical procedure. Particles could be stuck together by static and appear to be agglomerated when in fact they are separate particles. By measuring the particles greater than 105 μm , the static problems are reduced. For smaller particles, static can be reduced by first mixing the resin particles with an organic non-solvent such as ethanol or methanol, evaporating the solvent and then using the optical procedure. 45 x optical photomicrographs are prepared that can provide for a count of at least 400 particles for each sample. Using a Zeiss TGZ-3 Particle Analyzer, count the required number of particles by setting the counting aperture at the maximum diameter of the particle. This would form the circumscribed circle. Repeat the count on the same particles but use the minimum diameter of the aperture that will describe the minimum diameter of the particle. This would form the inscribed circle. The shape factor of the resin sample is determined by adding together the diameters of all the inscribed circles and dividing that number by the sum of all the circumscribed diameters. The shape factor for the resin represents an average of the particles in the sample.

Resin having particles with a high shape factor will have a higher bulk density than resin having particles with a lower shape factor assuming constant porosity and particle size. Very simply, spherical objects pack more tightly than do irregular objects. The resins of this invention preferably have a bulk density greater than 0.58 g/cm³ with the more preferred bulk density being greater than 0.62 g/cm³, when used in rigid applications such as pipe and siding. For resins used in flexible applications, the bulk density is preferably greater than 0.50 g/cm³. The lower bulk density for flexible applications resin is due to the higher porosity. The increased bulk density of spherical resins over non spherical resin results in increased shipping and storage efficiency, that is more weight of resin can be stored or shipped in a given container volume. Also, with other factors being constant, the increased bulk density and spherical shape result in increased extruder output, meaning more end product such as pipe can be produced on a given piece of extrusion equipment.

To further illustrate the present invention, the following specific examples are given. In the examples all parts and percents are by weight unless otherwise indicated.

EXAMPLE 1

The polymerization recipe employed was as follows:

50 In this example, a three-liter stainless steel reactor, equipped with agitation was employed. The water, dispersants, surfactants and catalysts were added to the reaction and agitated at 700 rpm. The vinyl chloride was then added and the contents heated to 57°C. During the course of the reaction, water was continuously added to the reactor to compensate for the shrinkage in volume due to the conversion of monomer to polymer. When the reaction was complete, further polymerization was stopped by the addition of bisphenol A shortstop. The contents of the reactor were emptied and the polymer recovered in the usual manner. The polymer was tested and the results are given in Table II. Average particle size was determined according to ASTM D 1705. DOP porosity was determined according to ASTM D 3367-75. Apparent bulk density and funnel flow time were determined according to ASTM D 1895.

This Example is presented to demonstrate that when the level of the high viscosity hydroxypropyl methyl cellulose of this invention is increased, there is further improvement in the bulk density. The recipe used was as shown in Table III.

TABLE I

Ingredient	Parts by Weight	
	Run 1	Run 2
Vinyl chloride monomer	100	100
Water (demineralized)	152	152
Peroxydicarbonate catalyst	0.0450	0.0450
Bisphenol A	0.0400	0.0400
Polyethylene oxide containing surfactant	0.0200	0.0200
Polyvinyl alcohol surfactant	0.0100	0.0100
Hydroxypropyl methyl cellulose		
viscosity 0.05 Pa.s	0.0800	-
viscosity 4 Pa.s	-	0.0800

The data from Runs 1 and 2 are shown in Table II.

TABLE II

Test	Resin	
	Run 1	Run 2
Avg. particle size (μm)	103.2	201.9
DOP Porosity (cm^3/g)	0.164	0.063
Apparent bulk density (g/cm^3)	0.489	0.753
Funnel Flow Time (sec.)	28.1	13.2

The above data of Table II show that the bulk density is much higher in Run 2 where the high viscosity (4 Pa.s) hydroxypropyl methyl cellulose was used compared with the same recipe having the lower viscosity (Run 1) material.

EXAMPLE 2

This Example is presented to show that a very high viscosity (75 Pa.s) hydroxypropyl methyl cellulose will make spherical particle resin having high bulk density. As can be seen from Run 3 below, it is preferred to use a higher amount of the novel dispersant as the viscosity of the novel dispersant increases. The reaction was run following the same procedures and conditions as in Example 1 except for the type and amount of hydroxypropyl methyl cellulose. The recipe used is as shown in Table III.

TABLE III

6	<u>Ingredient</u>	<u>Parts by Weight</u>	<u>Run 3</u>
	Vinyl choride monomer		100
	Water (demineralized)		152
10	Peroxydicarbonate catalyst		0.0450
	Bisphenol A		0.0400
	Polyethylene oxide containing surfactant		0.0200
15	Polyvinyl alcohol surfactant		0.0100
	Hydroxypropyl methyl cellulose viscosity 75 Pa.s		0.0800
20			

The data from Run 3 is shown in Table IV.

TABLE IV

25	<u>Test</u>	<u>Resin</u>	<u>Run 3</u>
	Avg. particle size (μm)		125.8
30	DOP Porosity (cm^3/g)		0.088
	Apparent bulk density (g/cm^3)		0.634
35	Funnel Flow Time (sec.)		15.5

From the above data it can be seen that the 75 Pa.s viscosity hydroxypropyl methyl cellulose requires a higher concentration than does the 4 Pa.s viscosity material, however, it does work very well in giving a high bulk density resin.

EXAMPLE 3

This Example is presented to show that the high viscosity hydroxypropyl methyl cellulose of this invention may be used alone as the only dispersant to produce a high bulk density spherical resin. The reaction was run the same as in Example 1. The recipe used was as follows:

TABLE V

<u>Ingredient</u>	<u>Parts by Weight</u>
	<u>Run 4</u>
Vinyl choride monomer	100
Water (demineralized)	152
Peroxydicarbonate catalyst	0.0450
Bisphenol A	0.0400
Polyethylene oxide containing surfactant	0.0200
Polyvinyl alcohol surfactant	0.0100
Hydroxypropyl methyl cellulose viscosity 4 Pa.s	0.0600

The properties of the resin produced in Run 4 are shown in Table VI.

TABLE VI

<u>Test</u>	<u>Run 4 Resin</u>
Avg. particle size (μm)	179.8
DOP Porosity (cm^3/g)	0.066
Apparent bulk density (g/cm^3)	0.695
Funnel Flow Time (sec.)	15.7

The results shown by Examples 1 through 3 are very surprising in that the viscosity of the hydroxypropyl methyl cellulose makes a large difference in the final resin. The higher viscosity materials produce a spherical resin having high bulk density. The high viscosity hydroxypropyl methyl cellulose can even be used as the only dispersant and produce a spherical, high bulk density resin.

The resins produced according to this invention are spherical in shape and can be obtained in a fused state.

The resins produced by this invention have many uses. They may be formulated with plasticizers, lubricants, stabilizers and impact modifiers and extruded into pipe, house siding, window frames and the like.

Claims

1. A process for producing spherical particles of polyvinyl chloride resin in the presence of a dispersant, characterized in that said dispersant is a hydroxypropyl methyl cellulose polymer having the formula:

TABLE V

<u>Ingredient</u>	<u>Parts by Weight</u>	
	<u>Run 4</u>	
Vinyl choride monomer	100	
Water (demineralized)	152	
Peroxydicarbonate catalyst	0.0450	
Bisphenol A	0.0400	
Polyethylene oxide containing surfactant	0.0200	
Polyvinyl alcohol surfactant	0.0100	
Hydroxypropyl methyl cellulose viscosity 4 Pa.s	0.0600	

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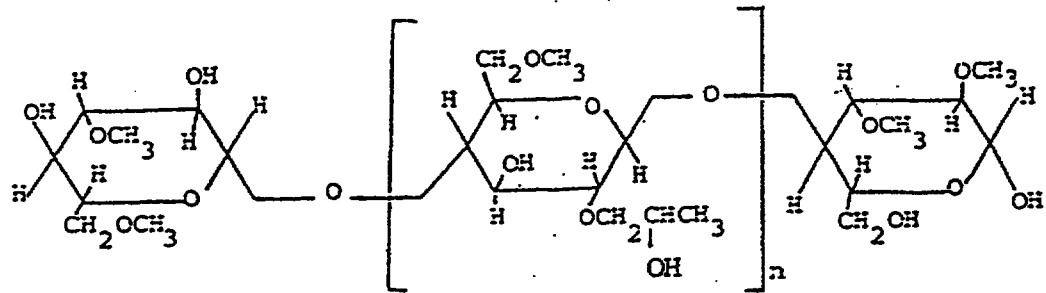
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The resins produced according to this invention are spherical in shape and can be obtained in a fused state.

The resins produced by this invention have many uses. They may be formulated with plasticizers, lubricants, stabilizers and impact modifiers and extruded into pipe, house siding, window frames and the like.

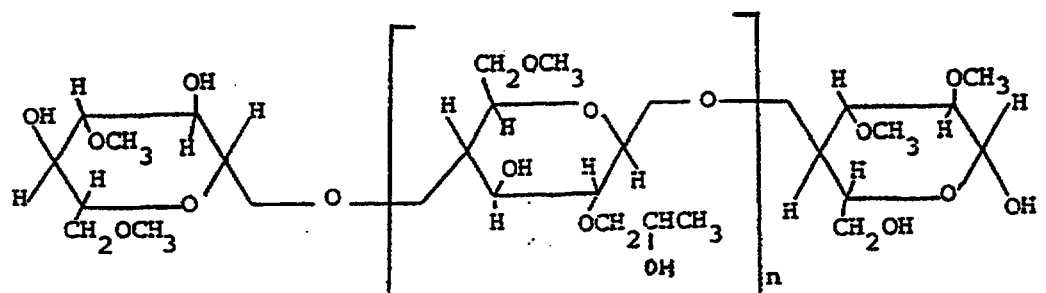
Claims

1. A process for producing spherical particles of polyvinyl chloride resin in the presence of a dispersant, characterized in that said dispersant is a hydroxypropyl methyl cellulose polymer having the formula:



15 wherein n is from 300 to 1500, said dispersant has a molecular weight of from 50,000 to 500,000, a viscosity of from 1 to 100 Pa.s as a 2% solution in waters at 20° C as measured by ASTM D 2363, said dispersant is employed in the range of from 0.02 to 0.1 part by weight said part by weight based on 100 parts by weight of polymerizable monomer, wherein said, polyvinyl chloride resin has a bulk density greater than 0.58 g/cm³ and a Dop porosity greater than 0.06 cm³/g.

2. A process of Claim 1 wherein said dispersant has a viscosity of from 2 to 10 Pa.s.
- 20 3. A process of Claims 1 to 2 wherein said polymerization is conducted at a temperature in the range of from 0° C to 100° C.
4. A process of Claims 1 to 3 wherein said polymerization is conducted in the presence of a monomer soluble free radical yielding catalyst.
- 25 5. A process of Claims 1 to 4 wherein said polymerization is conducted with agitation throughout the polymerization.
6. A process of Claims 1 to 5 wherein there is also present at least one surfactant selected from the group consisting of partially hydrolyzed polyvinyl acetate, methyl cellulose, polyethylene oxide containing surfactant, non-polyethylene oxide containing surfactant, sodium lauryl sulfonate, and low molecular weight hydroxypropyl methyl cellulose.
- 30 7. A spherical polyvinyl chloride resin in particulate form wherein the outside surface of said resin particles comprises hydroxypropyl methyl cellulose polymer having the formula:
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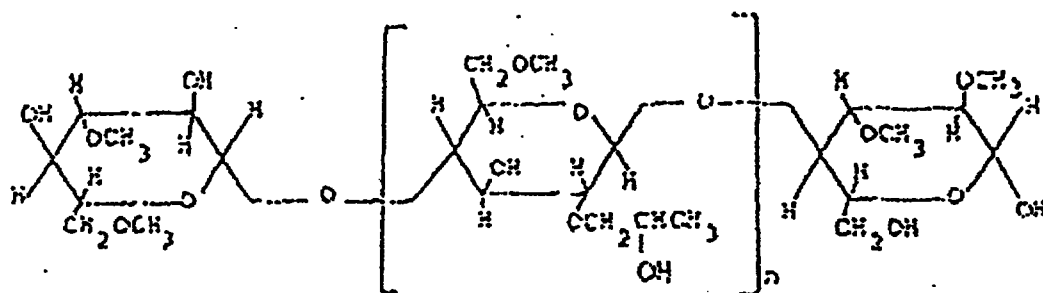
50 wherein n is from 300 to 1500 and wherein said dispersant has a molecular weight of from 50,000 to 500,000 and a viscosity of from 1 to 100 Pa.s as a 2% solution in water at 20° C as measured by ASTM D 2363.

8. A resin of Claim 7 wherein said resin has a bulk density greater than 0.58g/cm³ and a Dop porosity greater than 0.06 cm³/g.
- 55 9. A resin of Claims 7 and 8 in the fused state.

Revendications



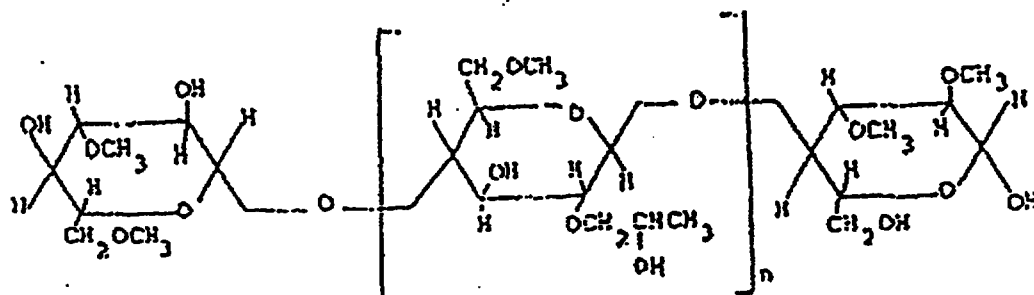
1. Procédé pour la préparation de particules sphériques de résine poly(chlorure de vinyle) en présence d'un dispersant, caractérisé en ce que ledit dispersant est un polymère hydroxypropylméthylcellulose correspondant à la formule



dans laquelle n est compris entre 300 et 1 500,

ledit dispersant a une moléculaire comprise entre 50 000 et 500 000, une viscosité comprise entre 1 et 100 Pa.s, sous forme d'une solution à 2% dans l'eau à 20 °C telle que mesurée selon ASTM D 2363, ledit dispersant est utilisé dans la plage de 0,02 à 0,1 partie en poids, pour 100 parties en poids de monomère polymérisable ladite résine poly(chlorure de vinyle) ayant une densité apparente supérieure à 0,58 g/cm³ et une porosité Dop supérieure à 0,06 cm³/g.

2. Procédé selon la revendication 1, dans lequel ledit dispersant a une viscosité comprise entre 2 et 10 Pa.s.
3. Procédé selon les revendication 1 et 2, dans lequel ladite polymérisation est effectuée à une température dans la plage de 0 à 100 °C.
4. Procédé selon les revendication 1 à 3, dans lequel ladite polymérisation est effectué en présence d'un catalyseur donnant des radicaux libres, soluble dans le monomère.
5. Procédé selon les revendication 1 à 4, dans lequel ladite polymérisation est effectuée avec agitation pendant toute la polymérisation.
6. Procédé selon les revendication 1 à 5, dans lequel est également présent au moins un agent tensioactif choisi parmi un poly(acétate de vinyle) partiellement hydrolysé la méthylcellulose, un agent tensioactif contenant du polyoxyéthylène, un agent tensioactif ne contenant pas de polyoxyéthylène, le laurylsulfonate de sodium et une hydroxypropylméthylcellulose à faible masse moléculaire.
7. Résine poly(chlorure de vinyle) sphérique sous forme particulaire, dans laquelle la surface externe desdites particules de résine comprend un polymère hydroxypropylméthylcellulose correspondant à la formule



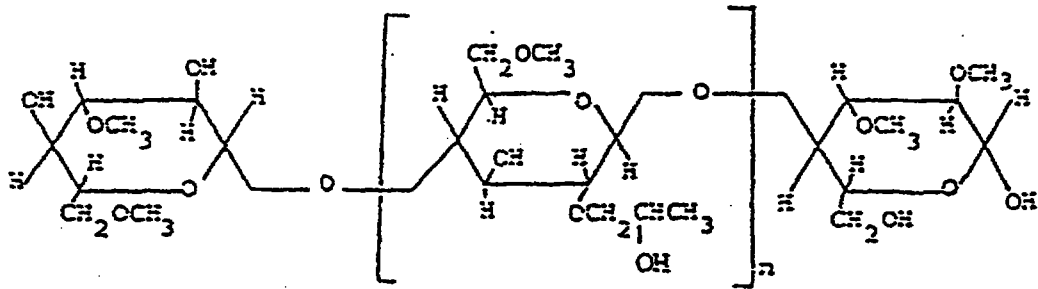
dans laquelle n est compris entre 300 et 1 500, et ledit dispersant a une masse moléculaire comprise entre 50 000 et 500 000 et une viscosité comprise entre 1 et 100 Pa.s, sous forme d'une solution à 2% dans de l'eau à 20 °C, telle que mesurée selon ASTM D 2363.



8. Résine selon la revendication 7, dans laquelle ladite résine a une densité apparente supérieure à 0,58 g/cm³ et une porosité Dop supérieure à 0,06 cm³/g.
9. Résine selon les revendication 7 et 8, à l'état fondu.

Ansprüche

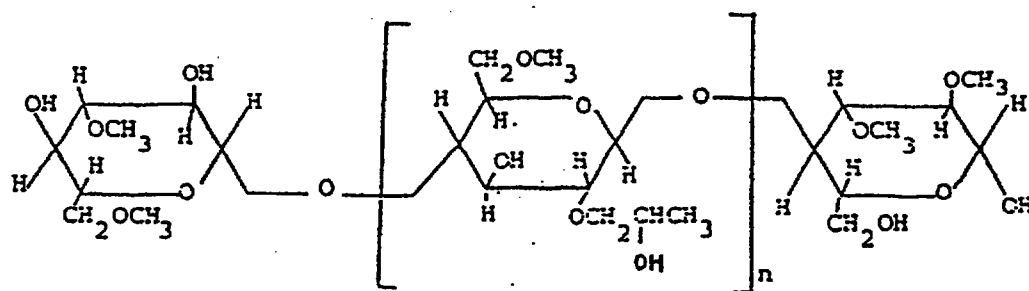
1. Verfahren zur Herstellung kugelförmiger Teilchen aus Polyvinylchlorid-Harz in Gegenwart eines Dispergiemittels, dadurch gekennzeichnet, daß das Dispergiemittel ein Hydroxypropylmethylcellulose-Polymer der Formel



ist, in der n 300 bis 1500 ist, und

das Dispergiemittel ein Molekulargewicht von 50 000 bis 500 000 und eine Viskosität von 1 bis 100 Pa.s, gemessen als 2-proz. Lösung in Wasser bei 20 °C nach ASTM D 2363, hat, das Dispergiemittel im Bereich von 0,02 bis 0,1 Gew.-Teile, bezogen auf 100 Gew.-Teile des polymerisierbaren Polymers eingesetzt wird, wobei das Polyvinylchlorid-Harz eine Schüttdichte, die größer als 0,58 g/cm³ ist, und eine DOP-Porosität, die größer als 0,06 g/cm³ ist, besitzt.

2. Verfahren nach Anspruch 1, worin das Dispergiemittel eine Viskosität von 2 bis 10 Pa.s hat.
3. Verfahren nach den Ansprüchen 1 bis 2, worin die Polymerisation bei einer Temperatur im Bereich von 0 °C bis 100 °C durchgeführt wird.
4. Verfahren nach den Ansprüchen 1 bis 3, worin die Polymerisation in Gegenwart eines monomer-löslichen, freie Radikale liefernden Katalysators durchgeführt wird.
5. Verfahren nach den Ansprüchen 1 bis 4, worin die Polymerisation unter Rühren während der gesamten Polymerisation durchgeführt wird.
6. Verfahren nach den Ansprüchen 1 bis 5, worin auch wenigstens ein Tensid anwesend ist, das aus der aus partiell hydrolysiertem Polyvinylacetat, Methylcellulose, einem Polyethylenoxid enthaltenden Tensid, einem nicht Polyethylenoxid enthaltenden Tensid, Natriumlaurylsulfonat und niedermolekularer Hydroxypropylmethylcellulose bestehenden Gruppe ausgewählt ist.
7. Kugelförmiges Polyvinylchlorid-Harz in Teilchen-Form, worin die äußere Oberfläche der Harz-Teilchen ein Hydroxypropylmethylcellulose-Polymer der Formel



umfaßt, in der n 300 bis 1500 ist, und in der das Dispergiermittel ein Molekulargewicht von 50 000 bis 500 000 und eine Viskosität von 1 bis 100 Pa.s, gemessen als 2-proz. Lösung in Wasser bei 20 °C nach ASTM D 2363, hat.

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8. Harz nach Anspruch 7, worin das Harz eine Schüttdichte, die größer als 0,58 g/cm³ ist, und eine DOP-Porosität, die größer als 0,06 g/cm³ ist, besitzt.
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9. Harz nach den Ansprüchen 7 und 8 im aufgeschmolzenen Zustand.