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METHOD OF INCREASING THE VISCOSITY OF POLYMERS

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Various methods are known for regulating the molecular weight of polymerized unsaturated compounds manifested by the viscosity of its solutions under special conditions. F. i. higher viscous polymers are obtained by polymerizing undiluted monomers as if starting from their solutions. The grade of polymerization is reduced much more already by small additions of substances as aldehydes, ketones and the like which have a specific influence on the course and the manner of the process of polymerization than by diluting with solvents. The grade of polymerization is the higher the fewer catalysts are allowed to act and the polymers obtained only by exposure to light or by irradiation have a special position. Higher molecular polymers are further obtained by interrupting the polymerization while a considerable part of the monomers is still existing unchanged. Specially high viscous polymers are obtained above all if the polymerization is executed in emulsion, preferably in a watery one, whereby, if necessary the emulsification by any suitable emulsifying agents, preferably by partially saponified derivates of polyvinyl alcohol, is not caused before a part of the monomers is already polymerized. The temperatures and pressures at which the polymerization is executed have also an influence on it specially if monomers of a low boiling point are applied.

Now there was found a means to increase the viscosity of the polymers under all conditions in a surprising manner. The process according to the invention principally consists in interrupting the polymerization of the monomers by cooling down if a considerable part is still unpolymerized, hereafter the thus obtained solution of raw polymers or raw emulsion is gradually heated anew until the unchanged monomer is evaporated. The time of heating must be considerably longer than that necessary for only separating the monomers.

This method is specially active if the subsequent heating is executed first for some time beneath the boiling point while the temperature is increased only later on above this boiling point whereby the pressure is gradually reduced.

The highest increase of viscosity is obtained by carrying out the subsequent heating in steps, in that way, that f.i. the temperature is kept first for some hours at 30°C, then at 40°, 50°, 70°, 90° C and about 95–100°C.

Example 1

1 kg of acetaldehyde was added to 300 kg of vinyl acetate and the vinyl compound was polymerized without an addition of a solvent until the polymerized part of the employed monomers amounted to about 40%. Hereafter the polymerization was interrupted by cooling down. A test of the solution of raw polymers diluted by vinyl acetate until a content of polymers of 20% yielded the viscosity of 0,5–0,6 at 20°C (measured according to the method of Hercules Powder).

The solution of raw polymers was now gradually heated, always for some hours to about 30°, 40°, 50°, 70°, 90°C and finally to about 95°C whereby the pressure was gradually reduced to the technical vacuum; thereby the distillation of the monomers was completed. The total process lasted for about 20 hours. The thus obtained polyvinyl acetate the quantity of which was not increased by the subsequent heating yielded a viscosity of 4, (solution of 20%).

Example 2

300 kg of vinyl acetate were partially polymerized according to example 1 whereby only 0.2 kg of acetaldehyde were added. A solution with 20% of raw polymers showed the viscosity 4. By subsequent heating according to example 1 the viscosity was increased to 200.

Example 3

Vinyl acetate without an addition of aldehydes yielded according to Example 1 a solution of raw polymers of the viscosity 7–8 after diluting to 20%. By subsequent heating according to the above examples a polyvinyl acetate of the extraordinary high viscosity of 10 000 was obtained.

These examples show that by the method of the invention not only surprisingly high viscosities can be obtained which are connected with excellent mechanical thermical and chemical properties of the polymers but that even relatively high viscosities can be also obtained by applying auxiliary methods which would lower the viscosity but modify the polymerization in various directions. F.i. a dilution with solvents and an addition of aldehydes are not to be applied if exspecially high viscosities are intended, but by the excellant efficiency of the method according to the invention, it is nevertheless possible to attain relatively high viscosities when the regulating and modifying effect of these additions upon the forming polymers is also applied. Expecially the known polymers, peculiarly modified by an addition of a large amount of aldehyde, may be obtained in a considerably higher molecular state. On the other hand the special polymers obtained by applying a large amount of catalysts may now

be obtained without giving up a relatively high viscosity.

By the method according to the invention it is also possible to increase considerably the efficiency of other methods which aim at high viscosities. F.i., the polymerization in emulsion in combination with the method according to the invention yields still higher viscosities than the polymerization in emulsion per se. The same is due to the polymerization effected by exposure to light resp. by irradiation or radiation.

The new method may be applied to the polymerization of all the unsaturated compounds being polymerizable to high molecular substances expecially to all kinds of aliphatic or aromatic vinyl compounds and esters and derivatives of acrylic acid and interpolymers of these substances. Fundamentally, it is necessary for the effect according to the invention that the solution or emulsion of raw-polymers being after-treated still contains a considerable amount of monomers. On the other hand also the modified polymers being formed by far-reaching polymerization of the applied monomers may be improved by this method. For this purpose monomers are added before or after the end of the polymerization. These added monomers may be the same as the polymerized one or they may be of other nature. Mixtures of various monomers may also be applied. F.i. monomer vinylacetate or acrylic acid or β-Oxydroxybutadiene and the like are added to a mixture of vinyl acids and vinyl chloride, nearly completely polymerized and then after-heating according to the invention may be applied to the modified raw polymers.

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