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METHOD FOR HARDENING OF POLYMERS

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The present invention relates to a method for hardening polymers.

When hardening polymerized natural or artificial substances having a structure with linear chain molecules, such as, for instance, polystyrene, polyacrylates, natural or synthetic rubber drawbacks are presented in two respects, since, on the one hand, some of these substances cannot be hardened at all by the methods hitherto known and on the other hand the hardening of polymers capable of being hardened by the usual vulcanization causes an impairment of the dielectric properties undesirable for some electrotechnic purposes, particularly owing to the absolutely undesirable increase of the loss angle and to the increase of the dielectric constant also undesirable in most cases.

According to the invention the polymerized natural or artificial substances, particularly having a structure with linear chain molecules, are hardened by the fact that these elements are homogeneously mixed with mixtures of substances still capable of being polymerized during the co-polymerization of which three-dimensional macromolecules are produced, and then the co-polymerization is effected. In this case the co-polymerization may be effected before or after giving the mixtures of substances the desired shape. These mixed polymers are produced, as a rule, by the polymerization of a mixture of at least two bodies capable of being polymerized with each other, of which at least one contains two groups capable of being polymerized. For instance, the following known mixtures of substances are capable of being polymerized: Styrene + divinylbenzol, acrylic acid ester + divinylbenzol or + divinylketone or + divinylether or + vinylpropenylbenzol, vinylether + divinylketone or + vinylpropenylbenzol.

By the invention substances or even shaped bodies may be surprisingly obtained which present properties particularly desirable in the field of artificial substances. By the invention the field of application of the mixed polymers consisting of three-dimensional macromolecules is at the same time considerably enlarged, since these mixed polymers are as is well known brittle, infusible and insoluble transparent substances, whose properties may be deduced from their three-dimensional molecular structure. These mixed polymers, particularly when being pressed and sprayed present in most cases considerable difficulties owing to their brittleness and infusibility. Also these difficulties are materially reduced or entirely avoided by the invention.

The substances or bodies produced according to the invention are harder than the basic substances polymerized and employed in the manufacture thereof; this may be called a pseudo-vulcanization. Furthermore, they are more tough and more resistant to heat but are insoluble and often only capable of swelling in the usual solvents (particularly in the aromatic hydrocarbons, such as benzol, toluene or xylene). A particular advantage of the invention consists in the fact that it is also possible to produce substances also capable of being fused and sprayed, the temperatures at which these substances are employed lying, of course, higher than that of the starting substances. A further essential advantage consists in the fact that the substances according to the invention do not age or at all events not to a greater extent than the starting substances and need not contain constituents which are not absolutely necessary to compose the same, i. e., particularly any filling substances, vulcanization accelerators or the like. If substances are to be produced with a particularly low dielectric loss angle, which is readily possible it is advisable to use starting substances which consist only of pure hydrocarbons or substances having a small total dipole moment.

It is possible to bring about any conditions whatever, depending upon the kind and the quantity of the homogeneous mixture of the starting substances subjected to the polymerization process. In this case it is particularly favorable that the co-polymerization of the starting substances still to be polymerized may be effected in the already polymerized starting substance even after giving the body to be produced from the final substance the desired shape, since in this manner a body may be produced in a soft state and may then be hardened only by the application of heat.

Example 1

75 parts by weight of polystyrene are homogeneously mixed with 25 parts by weight of a mixture consisting of styrene and 1% paradivinylbenzol, whereby a swelling is effected and polymerized for about 24 to 48 hours at a temperature of 130° centigrade. The transparent substance thus produced is highly resistant to shaping, does not tend to form cracks as does polystyrene and is capable of being sprayed. The softening point lies 10° centigrade above the softening point of the pure polystyrene employed.

Example 2

75 parts by weight of polyacrylic acid-isobutyl-

ester and 25 parts by weight of the mixture styrene + 1% paradivinylbenzol are homogeneously mixed, whereby a swelling is effected. The hardening mixture is then finally polymerized. The substance thus produced has approximately the properties inherent in slightly vulcanized rubber. If another mixing ratio is chosen, for instance, a ratio of 50 parts by weight to 50 parts by weight of the starting substances a no longer transparent leather-like substance is obtained.

Example 3

The mixture of 70 parts by weight of a highly polymeric substance known as Oppanol B 200 with 30 parts by weight of the mixture styrene+1% divinylbenzol produced on a mixing roller or on another mixing device, if necessary by the application of a moderate heat is polymerized by heating. Also this substance has a soft rubber-like character and it is possible to obtain leather-like substances also in this case by varying the mixing proportion of the starting material.

In the case of substances difficult to be mixed owing to their tenacity as intimate a mixture as possible may be obtained with the aid of other substances by the fact that these substances difficult to be mixed are so intensely undercooled that they may be finely divided and may be mixed in this state with the other substances.

When treating highly molecular substances having as above described a structure with linear chain molecules it may happen that these substances smear superficially during the polymerization process and become thereby defective. Such a smearing has not yet been observed when treating the highly molecular substances having a structure with linear chain molecules in another manner. This is probably due to the fact that the high molecular substances having a structure with linear chain molecules are dissolved when carrying out the method according to the invention and, consequently, may react very easily with the oxigen of the atmosphere surrounding the same.

This superficial smearing of the highly molecular substances when carrying out the method according to the invention is best avoided by the fact that the method according to the invention is carried out in an atmosphere free from or at least poor in oxigen. In this case by an atmosphere poor in oxigen is to be understood such an atmosphere in which the oxigen is only present up to an innoxious concentration.

The method according to the invention may, for instance, be carried out practically by the use of a vacuum, in which case a moderate vacuum is sufficient which, for instance, may be produced with the aid of a water-jet pump. Also inert gases, for instance, nitrogen and carbonic acid as well as water vapor may, however, be employed as a protective atmosphere. Furthermore, water itself may be utilized as an atmosphere containing slight amounts of oxigen. Such an atmosphere is preferable, for instance, when treating polyisobutylenes, polybutadienes, polyvinylethers and polyacrylates.

The method according to the invention presents particular advantages when used in the field of electrical engineering. The substances or bodies produced according to the invention may be employed for insulating purposes in various manners. For instance, electric conductors may be provided according to the invention with a covering applied thereto by any suitable spraying or pressing method. However, also parts of a device of a particularly complicated shape may be made to gauge without giving rise to a formation of cracks. The invention may also be used for the manufacture of semi-conductors by adding prior to the polymerization to the homogeneous mixture conducting or even only semi-conducting substances of the desired kind and in the desired amount.

The invention is not limited to the fact that only one polymerized basic substance or only one mixture capable of being polymerized is employed or that these components are pure, but the invention may also be used for hardening substances or mixtures of substances which contain not only one but also a plurality of polymerized components and furthermore not only pure components but also mixed with other substances such as, for instance, softening agents, stretching agents etc. Also in the manufacture and treatment of mixtures of substances capable of being polymerized the components may be combined in any desired manner, number and sequence. Particularly, it is also possible to combine the components of the final substance (total mixture) in various steps and, if desired, to polymerize the same in various steps.

The invention presents the further advantage that the substances produced according to the method of the invention from basic substances capable of being vulcanized may be subjected after the co-polymerization to a further vulcanization, since it has been surprisingly found that the vulcanization of these substances requires so small amounts of vulcanizing agents that the dielectric properties of the materials are thereby affected only to a very slight extent, while the mechanical properties are improved to the same extent as is possible only with the aid of great amounts of vulcanizing agents when employing such substances which are vulcanized without the use of the method according to the invention. The particular advantage of the method according to the invention consists in the fact that substances are thereby produced which not only present on the one hand very good dielectric properties and on the other hand mechanical properties not hitherto attained, but are in practice at the same time sufficiently resistant to heat, since the method according to the invention may be readily carried out in such a manner that the bodies produced in any thermoplastic condition are rendered free from the thermoplasticity in the desired manner by the vulcanization.

The improvement attained by the vulcanization is apparent from the fact that the tensile strength of a substance containing natural rubber as a basic substance and produced according to the method of the invention by the use of a mixed polymer consisting of styrene and divinylbenzol is increased by the vulcanization from 105 kg/cm² and 70% elongation to 170 kg/cm² and more than 450% elongation. In this case the quantity of sulphur (referred to the percentage of rubber) required for the vulcanization amounts only to 1% and less. Such high values of the tensile strength and elongation have hitherto only been attained in substances containing natural rubber as a basic substance if considerably higher degrees of vulcanization (i. e., for instance, as usual 3% sulphur) have been employed, in which case, however, a smaller hardness had to be put up with.

It must be particularly pointed out that the vulcanization may be carried out in the case of all substances capable of being vulcanized and produced according to the invention, i. e., not only in the case of substances containing natural rubber as a basic substance, but also in the case of such substances containing artificial rubber. If natural rubber be employed it is preferable to render it free from, or at least poor in, protein before vulcanizing it, for which purpose various methods are known and have proved satisfactory in practice.

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