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FORMATION BY IRRADIATION OF AN EXPANDED, CELLULAR, POLYMERIC BODY

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1 Claim. (Cl. 204—158)

This invention relates to the treatment of polymeric esters of methacrylic acid.

When exposed to penetrating ionising radiation these esters undergo a process of disintegration. At first there is no visible evidence of such disintegration apart from a slight colour change but gradually small bubbles appear within the substance. As the irradiation is continued there is a rapid increase in the number and size of the bubbles and the material expands and becomes wholly cellular. Finally the cellular mass breaks down into a powder. The expanded cellular mass produced before breakdown tends to be friable.

An object of the present invention is to provide a process for producing from the aforesaid polymeric esters a cellular expanded material having useful mechanical strength and good dielectric properties.

The invention is based on the discovery that if irradiation is carried out below the softening point of the material, no bubbles are formed in a surface layer and that by suitable selection of the irradiation dose and the temperature of a subsequent heat treatment a bubble free outer skin derived from this surface layer is formed and that a strong cellular mass develops within the skin which sets hard and smooth.

The nature of the invention is such that it is applicable only to those polymeric esters of methacrylic acid having a softening point above 40° C. and such esters will be referred to as high softening point esters. The softening point of these esters is discussed by Wakeman on pages 469 and 470 in "Chemistry of Commercial Plastics," Reinhold Publishing Corporation, New York, 1947.

In accordance with the present invention a body of a polymeric ester of methacrylic acid having a softening point above 40° C. is subjected at a temperature below the softening point to a dose of penetrating ionising radiation sufficient to cause substantial polymer breakdown but insufficient to produce any visible effect apart from colour change and is then heated at a temperature above the softening point to effect expansion.

The invention may be further stated as a method of treating a body of a polymeric ester of a methacrylic acid having a softening point above 40° C. wherein the body is subjected at a temperature below its softening point to a dose of at least 5×10^6 Roentgens of penetrating ionising radiation until its average molecular weight is reduced to a value within the range 3×10^3 to 10^4 and is then heated at a temperature within the range 0 to 10° C. above its softening point to effect expansion.

The amount of radiation required to reduce the molecular weight to within the range above stated is dependant on the temperature, below the softening point, of the material during irradiation, a greater dose being required at lower temperatures. The larger the dose, the greater is the number of disintegrations and consequent bubbles and therefore to obtain an expanded material of close texture, a large dose is given at a low temperature.

The change in molecular weight may be readily deter-

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mined by measuring the change in viscosity of a sample in solution.

The product of the invention is mechanically strong and has a moisture resistant skin with a hard smooth surface. During the process of irradiation it is found that the volatile products of disintegration diffuse through a distance of about 1 mm. so that a boundary zone of this depth remains free from bubbles or latent bubbles and none are formed on subsequent heating. The depth of the skin is the depth of this free zone as reduced by stretching due to the expansion of the cellular core. It will be apparent that the invention is not applicable to the specimens in which the free zone would constitute the major volume.

The expansion ratio is regulated by the temperature of the heat treatment within the range of about 10° C. above the softening point and by the period of heating which is also varied as the size of the specimen. Preferably the heat treatment temperature is selected such that heating may be continued until a state of equilibrium is reached between the gas pressure and the tension in the softened mass when no further expansion takes place.

The invention may be carried out with plasticised or unplasticised material. In the case of polymethylmethacrylate, for example, the effect of adding 5% dibutyl phthalate as a plasticiser is to decrease slightly the dose required to reduce the molecular weight to within the given range and to decrease by about 5° the optimum temperature for obtaining a given expansion ratio.

The radiation requires to be of sufficient penetrative power to ionise the specimen uniformly throughout its depth and of sufficient strength to reduce molecular weight sufficiently within a practical time. A nuclear reactor provides a suitable source unless an irradiation temperature less than that obtaining in the reactor is required. The preferred source is a high energy artificial radioactive gamma emitting isotope such as cobalt 60 in relation to which the specimen may be readily maintained at any desired temperature.

Expansion is found to take place substantially uniformly so that a shaped article of the expanded substance may be formed by expanding a piece of say, polymethyl methacrylate shaped to represent a scale model of the final article. If slightly different expansion ratios are found to take place on different axes this may be suitably compensated by varying the dimensions of the model.

The process of the invention may, however, be carried out on a substance contained in a mould so that the swelling causes the substance to fill the mould and attain a desired final shape. In another particularly advantageous application of the invention the substance constitutes the dielectric of an electrical cable and is processed according to the invention in situ. Before processing, the substance may be a loose fitting sleeve, the process of the invention causing it to expand and occupy the void.

The following are examples of ways of carrying the invention into effect.

Example I

A $\frac{1}{2}$ in. diam. rod of unplasticised polymethyl methacrylate having a softening point of 125° C. was irradiated in a nuclear reactor at 75° C. until it had received a dose of 24×10^6 Roentgen. The dose produced no visible effect beyond change of colour to pale yellow. The molecular weight after irradiation as measured by an Oswald viscounter using a solution of the sample in chloroform was 5×10^4 . The rod was then heated for one hour at 130° C. Bubbles of gas were formed inside the rod which increased in size and expanded the rod until it was 6 times its original volume without rupturing the smooth outer skin.

Example II

A ½ in. diam. rod of polymethyl methacrylate plasticised with di-butyl phthalate and having a softening point of 120° C. was irradiated under the same conditions and with the same dose as Example I. Again there was no visible effect other than colour change. It was then heated at 125° C. for ¾ hour and a volume expansion of 7 times obtained.

Example III

A rod similar to that of Example II with a softening point of 120° C. was given a dose of 16×10^6 Roentgen at a temperature of 20 C. by means of a cobalt 60 source. The molecular weight was found to have fallen to 8×10^4 and there were no visible effects other than colour change. The rod was then heated at 130° C. for one hour and the rod expanded six times its original volume without rupture of the skin.

We claim:

A method of treating a body of a polymeric ester of a methacrylic acid having a softening point above 40° C.

to form an expanded cellular mass having a smooth skin comprising subjecting the body at a temperature below the softening point to a dose of at least 5×10^6 Roentgen of gamma radiation from a cobalt 60 source until its average molecular weight is reduced to a value within the range 3×10^5 to 10^4 and heating at a temperature within the range 0 to 10° C. above its softening point to effect expansion.

References Cited in the file of this patent

UNITED STATES PATENTS

2,045,651	Hill	June 30, 1936
2,697,255	Lindermann	Dec. 21, 1954

OTHER REFERENCES

U. S. Atomic Energy Commission, ORNL 928 (1951).
 O. Sisman et al., June 29, 1951, pages 8-10, 18-26, 28-32. Copy available from Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 "Nature," vol. 168 (pages 644, 645), 1951.