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MANUFACTURE OF SHEETS OR FILMS OF
ARTIFICIAL MATERIAL

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My present invention relates to a manufacture of sheets or films from polymerization products.

The manufacture of sheets or films from homogeneous and heterogeneous polymerisates of vinyl alcohol and its derivatives and of acrylic acid and its derivatives by the rolling process, that is to say, without the use of a solvent permits only to produce material of the minimum thickness of about 0.1 mm. It is usual to make thin sheets or films from, for example, cellulose esters or ethers, by dissolving the material in a suitable solvent and casting the solution to produce the sheet or film. The application of this process to the aforesaid artificial highly polymeric compounds, particularly to the mixed polymerisates from vinyl chloride and acrylic acid esters or its nitrile is, indeed, possible, but is too expensive owing to the large proportion of solvent required.

It is therefore an object of the present invention to provide a process of producing sheets and films from the aforesaid polymerization products, which is inexpensive to carry out and in which only a minimum of solvent need be employed.

A further object of the invention is to provide a process by which sheets or films having a thickness below 0.1 mm. may be obtained.

Further objects will become apparent from the following detailed description.

We have found that it is possible to produce sheets or films which are of a thickness below 0.1 mm., and indeed essentially thinner than this, from the homogeneous and heterogeneous artificial polymerisates, particularly the mixed polymerisates from vinyl chloride and acrylic acid without casting the film forming material from a solution. As suitable polymerisates may be mentioned polyvinyl halides for instance, polyvinyl chloride, or polyvinyl chloride which has been after-chlorinated, polyvinylacetate, polyvinyl propionate, polyvinyl butyrate, polymerisation products of mixtures of the monomeric substances or mixtures of these polymerisation products, for instance, of vinyl chloride and vinyl acetate, furthermore polymerisation products of mixtures of vinyl chloride with acrylic acid derivatives, for instance, esters of acrylic acid or its nitrile; also mixtures of polyvinylchloride with after-chlorinated polyvinylchloride. According to one modification of the invention the pulverulent artificial polymerisate is mixed with about 10 per cent of its weight of a true solvent for the polymerisate, for example acetone or a mixture of acetone and benzene, and this mixture of powder and solvent is rolled at a suitable

temperature. Further suitable solvents are methylene chloride, chloroform, toluene, mixtures of acetone with methylene chloride and toluene, or of toluene with methylene chloride, homologues of these compounds, cyclohexanone and monochlorobenzene. Owing to the presence of this small proportion of true solvent the softening point of the polymerisate is so far lowered that the rolling can reduce the thickness of the sheet below 0.1 mm. without any difficulty. By a heat-treatment the solvent may be removed from the sheets thus produced. By adding in small proportion amounting to 1 per cent or less of the polymerisate, one or more suitable softening agents, for instance, the esters of phthalic acid, the butyl ester of oleic acid, the benzoate of the alcohols obtainable from the cocoa nut fatty acids, tributylphosphate, trichlorethylphosphate and mixtures of these substances, the production of very thin sheets is facilitated without influencing essentially the softening point of the finished product.

The esters of phthalic acid have a good gelatinizing power and the benzoate of the alcohols obtainable from the cocoa nut fatty acids have a weak gelatinizing power on the polymerization products; the other softening agents have no solvent power.

According to another modification it has been found that the above polymerization products can also be made into sheets or films by mixing them with a suitable amount of a softening agent or a mixture of softening agents which may dissolve or not dissolve the polymerization product and subjecting them to a treatment on heated rollers. The amount of softening agent is selected according to the properties of the polymerization product and according to the condition in the rolling treatment. A polymerization product having a high softening point needs a relatively great addition of softening agent in order to obtain the required depression of the softening point, which is the necessary condition for producing sheets or films having a thickness inferior to 0.10 millimeter by a rolling treatment. When working up a polymerization product with a low softening point it is necessary to add only a few per cent of softening agent for obtaining the desired effect. As softening agents there may be used those above mentioned. Because of the low volatility of the softening agents they are not removed in the treatment on the heated rollers or by a drying process, but it is necessary to extract the sheets or films with an indifferent solvent, that is to say, a solvent which dissolves the soft-

ening agent but does not dissolve the polymerization product. This treatment lasts until the addition of softening agent is removed from the sheets of polymerization product; thus, the valuable properties of the original polymerization product are revived in the final product.

The treatment of the polymerization products according to this invention is carried out at a temperature between 100 and 150° C. preferably at a temperature of 120 to 125° C. Often it is desirable to maintain a very short interval of 3° C.

The following examples serve to illustrate the invention:

Example 1.—500 grams of powdered polyvinylchloride are mixed with 50 grams of acetone and the mixture is made into a sheet of 0.05 millimeter thickness by rolling the polymerization product for ½ hour on a roller frame provided with 3 rollers heated at 122 to 125° C. The softening point of the sheet is 81° C.

Example 2.—500 grams of powdered polymerization product from a mixture of vinylchloride and acrylic acid methylester (80:20) are intimately mixed with 45 grams of a mixture of acetone and benzene. This pulverulent product is made into a sheet of 0.05 millimeter thickness by a rolling treatment on two rollers heated at 130 to 135° C. The softening point of the sheet is about 68° C.

Example 3.—500 grams of a powdered polymerization product from a mixture of vinylchloride and vinylacetate are mixed with 50 grams of methylene chloride and toluene mixed in the ratio of 1:1 and made into a sheet of 0.02 millimeter thickness by a rolling treatment on a roller frame provided with 3 rollers heated at a temperature of 115 to 120° C.

Example 4.—500 grams of a powdered mixture of polyvinylchloride and after-chlorinated polyvinylchloride are mixed with 30 grams of a mixture of toluene and cyclohexanone (5:1) and subjected to a rolling treatment at 130 to 135° C. for producing a sheet of 0.02 millimeter thickness. The softening point of the sheet is about 70° C.

Example 5.—500 grams of a powdered polymerization product from a mixture of vinylchloride and acrylic acid nitrile are mixed with 5 grams of phthalic acid dibutylester and a mixture of 45 grams of acetone and benzene (1:1) and subjected to a rolling treatment at a temperature of 120 to 122° C. There are obtained sheets of 0.07 millimeter thickness.

Example 6.—500 grams of a powdered polymerization product from a mixture of vinylchloride and acrylic acid methylester (60:40) are rolled at 115° to a sheet of 0.05 millimeter thickness after the addition of a mixture of 47.5 grams of methylene chloride and toluene (1:1) and 2.5 grams of butyl oleate. The softening point of the sheet is 70° C.

Example 7.—500 grams of polyvinylchloride are intimately mixed with 50 grams of phthalic acid dibutylester and rolled on a roller frame provided with two rollers heated at a temperature of 110 to 115° C. to a sheet of 0.03 millimeter thickness. During this treatment the sheet loses 40 per cent of the added quantity of softening agent. The remainder of softening agent is removed by an extraction lasting 15 hours with a mixture of aliphatic hydrocarbons having a boiling point of 60 to 100° C. The finished sheet has a softening point of 78° C.

Example 8.—500 grams of a mixed polymer-

ization product from a mixture of vinylchloride and acrylic acid methylester (60:40) are mixed with 35 grams of phthalic acid ethylester and rolled on three rollers heated at 110 to 115° C. to a sheet of 0.05 millimeter thickness. In this treatment the sheet loses about 55 per cent of the added softening agent; by immersing the sheet in ether at room temperature for 24 hours the remainder of softening agent is removed. Hereafter the sheet has a softening point of 62° C.

Example 9.—500 grams of after-chlorinated polyvinylchloride are mixed with 50 grams of butyl oleate and rolled to a sheet of 0.07 millimeter at 125 to 128° C., whereby 60 per cent of the softening agent are removed from the sheet. The remainder of butyl oleate is removed by extraction with methanol in an extraction vessel, whereby the softening point is raised to 83° C.

The sheets made according to this invention may be used as a wrapping material for any desired purpose if desired after imprinting patterns or descriptions. They may also be used for lining plane objects for beautifying purposes or for stabilizing these objects which may be textiles, paper, card-board, metal foils, for instance, aluminium foils or gold foils for cigaret tips. On account of their great tensile strength and elasticity the sheets may be used as an aeroplane roofing material or the like. Their ductility and absolute water-proofness and light-proofness makes these sheets suited for the production of artificial leather and particularly for the upper covering layers. From the uncolored and colored sheets which may be provided with patterns or may be delustered, narrow ribbons or artificial flowers may be made.

A particular important technical application resides in the good insulating properties of the described sheets.

What I claim is:

1. In a process of producing sheets thinner than 0.1 mm. having a high softening point from a powdered polymerization product selected from the group consisting of polymerized vinyl compounds, polymerized acrylic acid esters, polymerized acrylic acid nitriles, mixed polymerizates comprising a vinyl compound and mixtures of these polymeric substances, the steps which comprise temporarily lowering the softening point of said product by adding up to about 10 per cent of a solvent selected from the group consisting of acetone, benzene, methylene-chloride, toluene, cyclohexanone, monochlorobenzene and mixtures of these solvents, and subjecting the mixture to a treatment on rollers heated to 100°–150° C.

2. In a process of producing sheets thinner than 0.1 mm. having a high softening point from a powdered polymerization product selected from the group consisting of polymerized vinyl compounds, polymerized acrylic acid esters, polymerized acrylic acid nitriles, mixed polymerizates comprising a vinyl compound and mixtures of these polymeric substances, the steps which comprise temporarily lowering the softening point of said product by adding up to about 10 per cent of a true volatile solvent and about 1 per cent of a softening agent and subjecting the mixture to a treatment on rollers heated to 100°–150° C.

3. In a process of producing a sheet of a thickness of 0.03 mm. from 500 parts by weight of powdered polyvinylchloride, the steps which comprise temporarily lowering the softening point of said polyvinylchloride by adding 50 parts by weight of phthalic acid dibutyl ester, subjecting

the mixture to a treatment on rollers heated to from about 110° C. to about 115° C. and extracting the remaining phthalic acid dibutyl ester by means of an aliphatic hydrocarbon having a boiling point of from 60 to 100° C.

4. In a process of producing a sheet of 0.05 mm. thickness from 500 parts by weight of powdered polyvinylchloride, the steps of lowering the softening point of said product by addition of 50 parts by weight of acetone and subjecting the mixture to a treatment on rollers heated to from 122 to 125° C.

5. In a process of producing a sheet of 0.05 mm. thickness from 500 parts by weight of a powdered polymerization product from a mixture of approximately 80% of vinyl chloride and approximately 20% of acrylic acid methyl ester, the steps which comprise temporarily lowering the softening point of said product by adding 45 parts by weight of a mixture of acetone and benzene and subjecting the mixture to a treatment on rollers heated to from 130 to 133° C.

6. In a process of producing sheets thinner than 0.1 mm. and having a high softening point from a powdered polymerization product selected from the group consisting of polymerized vinyl compounds, polymerized acrylic acid esters, polymerized acrylic acid nitriles, mixed polymerizates comprising a vinyl compound and mixtures of these polymeric substances, the steps which comprise temporarily lowering the softening point of said product by adding up to about 10% of a true volatile solvent to the powdered product, subjecting the still powdery mixture to a treatment on heated rollers and removing the volatile solvent from the sheet.

7. A treatment as defined in claim 6 wherein a softening agent is added to the powdered mixture of the polymerization product and the true

volatile solvent in a proportion incapable of gelatinizing the polymerization product before subjecting the resultant powdery mixture to the treatment on heated rollers.

8. In a process of producing sheets thinner than 0.1 mm. and having a high softening point from a powdered polymerization product selected from the group consisting of polymerized vinyl compounds, polymerized acrylic acid esters, polymerized acrylic acid nitriles, mixed polymerizates comprising a vinyl compound and mixtures of these polymeric substances, the steps which comprise temporarily lowering the softening point of said product by adding to the powdered product up to about 10 per cent of a softening agent selected from the group consisting of esters of phthalic acid, the butyl ester of oleic acid, the benzoate of the alcohols obtainable from the coconut fatty acids, tributyl phosphate, trichloroethylphosphate and mixtures of these substances, subjecting the powdered mixture to a treatment on heated rollers and removing residual amounts of the softening agent from the resulting sheet.

9. In a process of producing sheets thinner than 0.1 mm. having a high softening point from a powdered polymerization product selected from the group consisting of polymerized vinyl compounds, polymerized acrylic acid esters, polymerized acrylic acid nitriles, mixed polymerizates comprising a vinyl compound and mixtures of these polymeric substances, the steps which comprise temporarily lowering the softening point of said product by adding to the powdered product up to about 10% of a true volatile solvent and subjecting the still powdery mixture to a treatment on rollers heated to from about 100° to about 150° C.

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