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EXTRUSION OF PLASTICIZED CELLULOSE ACETATE

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This invention relates to extrusion and especially to a method of extruding cellulose acetate compositions to produce articles of pre-determined dimensions.

The hot extrusion of cellulose derivative compositions containing a plasticiser but no volatile solvent to make rigid or flexible articles of various cross-sections, e. g. rods, tubes and strips of rectangular or other cross-section is well-known. The extruded products such as thick-walled tubes, resulting from this process, however, undergo distortion and dimensional change on leaving the die. In consequence, thick-walled tubes made by this process, are far from circular in cross-section, even when the greatest care is taken to ensure that the central plug of the tube die is accurately centered. For some purposes, e. g. when the tubing is required for blow-moulding, this lack of circularity is no disadvantage. For certain other purposes, however, for instance for providing piping, feed tubes in automatic machines, cylindrical container bodies and sleeving for covering metal rods, there has long been a demand for rigid tubing of truly circular cross-section and of predetermined dimensions. Various methods have been described for obtaining tubes of the desired character by solventless extrusion of cellulose derivative compositions. G. Jargstorff and C. Joslin in "Modern Plastics," volume 26 (No. 1), pages 191–193 and 290, have referred to some of the difficulties encountered in designing and operating apparatus for attaining this end, and have described an apparatus in which these defects are to some extent overcome. In this apparatus, the tube emerging from the die is caused to pass through a tubular finishing die spaced apart from the extrusion die by a short heat-insulating connection and cooled by water jacket. The extruded tube is prevented from sticking to the said connection by blowing air into the annular space between the connection and the tube and is inflated so that its outer surface conforms to the inner surface of the finishing die by a second stream of air. The apparatus is necessarily complex and the authors indicate that very careful pressure control of the two air streams is necessary if the extruded tube is to be prevented both from ballooning out after leaving the finishing die and from expanding back against the extrusion die. In an alternative method described in British Patent No. 563,121 (a communication from the Plax Corporation), the plastic composition is extruded through a very long die (the examples specify dies over 10 ft. long) during passage through which it undergoes progressive cooling. The resistance to passage through this long die is very considerable and a necessary feature of the process is to maintain a continuous film of lubricant between the extruded material and the die surface. The continuous supply of this lubricant at the necessary pressure and in the necessary amount, involves the use of complex apparatus. Moreover, the fact that the tube obtained carries a coating of oil is a disadvantage in that any scrap made in operating the process cannot easily be re-used. U. S.

Patent No. 2,491,589 (C. E. Slaughter) proposes to obtain the desired effect by inflating the tube with air while its free end is blocked by a plug, and rapidly cooling the tube in a water bath. Besides the difficulty of supporting the plug inside the tube and of arranging that it provides the desired air-resistance, the passage of the hot tube through a water-bath introduces an undesirable complication, the surface of the tube is marred by contact with the water, it is difficult to inflate the tube sufficiently within the bath without undue inflation between the die and the bath and to avoid undue cooling of the die by the bath. The primary object of the present invention is to provide a simple method of making thick-walled tubes and other extruded products to predetermined dimensions, which is free from the disadvantages of such prior methods.

It appeared to us that the defects encountered in attempting to make tubes and other extruded products having the desired characteristics by the established method of solventless extrusion were, to a great extent, bound up with the fact that in these methods the extruded product leaves the extrusion die at a temperature at which it is still highly plastic. We attempted, therefore, to reduce the temperature of extrusion to a point at which the extruded product emerged from the die at a temperature below its heat-softening point. With compositions such as are normally used, e. g. compositions containing cellulose acetate plasticised with 40 to 50% of its weight of diethyl phthalate or a mixture of dimethyl phthalate and triphenyl phosphate in the ratio of 3:1, it was found that a coherent extruded product could not be obtained at such temperatures under any pressure that the normal screw extruder would stand. Trials with ram extruders were no more successful. We therefore attempted to reduce the pressure required, by incorporating various substances having lubricating properties. A further difficulty was then encountered, viz. that the lubricant marred the surface of the extruded product. Eventually we found that by incorporating with the plasticised cellulose acetate a small proportion, e. g. 1–5% by weight, of ricinoleic acid, this difficulty could be overcome. Very satisfactory products were obtained, for example, by extrusion of such compositions from a ram extruder provided with a tube die, the temperature in the extruder barrel being sufficiently high to ensure complete coalescence of the particles of the composition before reaching the die, and the forward end of the die being kept at a temperature sufficiently low to preclude change in dimensions of the extruded article (apart from thermal contraction) after leaving the die. Of many substances tried as alternatives to ricinoleic acid the best was found to be oleic acid but this was much inferior owing apparently to inferior compatibility. The products made with it were less homogeneous and it tended to sweat out of them. It is not therefore to be regarded as equivalent to ricinoleic acid.

The process of the present invention, therefore comprises feeding a plasticised cellulose acetate containing 1 to 5%, based on the cellulose acetate, of ricinoleic acid, in particulate form, into a heated chamber, forcing the composition through said chamber and extruding it therefrom through an appropriably shaped orifice into the air, and maintaining along the path of the composition up to the extrusion point a temperature gradient such that complete coalescence of the particles occurs before reaching said point, while at said point the extruded material is sufficiently cool to emerge as a self supporting article that, apart from thermal contraction, retains the dimensions imparted by the orifice.

Preferably the temperature of the composition in the course of its travel gradually reaches a maximum from which it declines rapidly. The maximum temperature reached along the path of the material must, of course,

be above the heat-distortion point of the material and it is of advantage for the temperature at the rear end of the extruder barrel to be somewhat above that point. The temperature at the forward end of the die should be below the heat-distortion point of material and is preferably not substantially above atmospheric temperature. The maximum temperature may be at or near the inlet but is preferably reached at a point nearer the outlet. The temperature along the path of the material declines from the point of maximum temperature to the outlet. We prefer to operate so that there is a gradual temperature rise from the inlet to near the outlet (e. g. to the rear end of the die) followed by a rapid temperature fall to the outlet at the forward end of the die. Suitable temperatures when working with a composition comprising cellulose acetate of acetic acid content 52.5 to 53.5 and viscosity 30 to 48 C. P. S. plasticised with 40 to 50% of its weight of diethyl phthalate or the equivalent, and containing 1 to 5% of ricinoleic acid are:

	° C.
Rear end of barrel (feed point)	50– 70
Middle of barrel	90–110
Front end of barrel	100–110
Rear end of die	90–100
Front end of die (extrusion point)	20– 30

Compositions suitable for use in the process of the invention, comprising plasticised cellulose acetate together with 1 to 5% based on the cellulose acetate of ricinoleic are believed to be novel and form part of the present invention. The compositions may, of course, contain suitable pigments, dyes, and other effect materials.

The following examples illustrate the invention:

Example 1

A moulding powder was made of the following composition, all the parts being by weight:

100 parts of cellulose acetate of acetyl value 52.5 to 53.5 (expressed as acetic acid) and giving a viscosity in 6% (by weight) solution in acetone at 25° C. of 36 C. P.
37.5 parts of dimethyl phthalate
12.5 parts of triphenyl phosphate
4 parts of ricinoleic acid

The moulding was charged into the rear end of a ram extruder provided with a tube die and with means for measuring and controlling the temperature at the points specified below.

The temperatures maintained were as follows:

	° C.
Rear end of barrel	50
Middle of barrel	90
Front of barrel	100
Rear of die	90
Front of die	25

Extrusion was affected at a rate of 5" per minute. In this way a tube of ¾" internal diameter, 1/16" thickness having an excellent finish was made. The regularity of the tube was such that it could be slipped on to steel rod of appropriate diameter to form a sliding fit.

Example 2

The process was carried out as described in Example 1 except that the plasticiser consisted of 50 parts of diethyl phthalate and the following temperatures were maintained:

	° C.
Rear end of barrel	70
Middle of barrel	110
Front end of barrel	110
Rear end of die	100
Front end of die	30

The acetyl value of the cellulose acetate used may be higher than 53.5, e. g. from 53.5 to 55.5. The viscosity of the cellulose acetate, however, should not be high and preferably should not exceed 60 C. P. or be below 30 C. P. when measured in 6% acetone solution at 25° C. We have obtained the best results with cellulose acetates of viscosity between 30 and 48 C. P.

The temperature specified can be varied to some extent but the temperature at which the material emerges from the die must be below the flow-temperature of the material and preferably below the heat-distortion temperature thereof (these temperatures being determined by the appropriate ASTM methods). The inlet should preferably be kept above the heat-distortion temperature and may be also above the flow temperature.

The invention has been described with particular reference to the making of rigid cylindrical tubes but by the use of dies of appropriate form other extruded sections can be made, e. g. tubes or rods of elliptical, square, rectangular or other cross sections, including bars of L-, U-, V-, T- and H-sections. These articles (and also cylindrical rods) can be made to high precision by the process of the invention.

The cellulose acetate must, of course, be plasticised. For cellulose acetates of acetic acid content up to about 56%, the plasticisers that can be used include (apart from those specified above) di- (methoxy ethyl) phthalate, methyl phthalyl ethyl glycolate, ethyl phthalyl ethyl glycolate, acetyl triethyl citrate, tri-(mono-chlorethyl) phosphate, tri-cresyl phosphate and the N-ethyl toluene sulphonamides. It will be understood that when a plasticiser of low compatibility for the cellulose acetate, e. g. triphenyl phosphate or tricresyl phosphate, is included the composition should also contain a greater proportion of a plasticiser of high compatibility. The content of ricinoleic acid may range from 1 to 5% based on the weight of cellulose acetate, and is preferably 3 to 4% of that weight.

Having described our invention, what we desire to secure by Letters Patent is:

1. Process for making articles by extrusion which comprises feeding a composition having a basis of plasticized cellulose acetate, said cellulose acetate containing 52.5–55.5% of combined acetic acid and having a viscosity in 6% by weight solution in acetone of 30–48 C. P. S. at 25° C., said composition being in particulate form, substantially free from any volatile liquid and containing 3–4%, based on the weight of cellulose acetate, of ricinoleic acid, into a heated chamber and extruding it therefrom through an appropriately shaped orifice into the air, the temperature of said chamber being from 50–70° C. at the feed point and 20–30° C. at the extrusion point, and being 100–110° C. at a point between the feed point and the extrusion point.

2. Process according to claim 1, wherein the cellulose acetate is plasticised with 40–50% of its weight of diethyl phthalate.

3. Process according to claim 1, wherein the cellulose acetate is plasticized with 40–50% of its weight of a mixture of dimethyl phthalate and triphenyl phosphate in the weight-ratio of 3:1.

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