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PROCESS FOR FORMING HOLLOW CELLULOSE ESTER ARTICLES

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This invention relates to the fabrication of objects from blanks of cellulose acetate or other organic thermoplastics that have been softened by soaking in water.

Many organic thermoplastics, notably those based on partial substitution products of cellulose, undergo some degree of softening when soaked in water. Advantage has been taken of this effect in fabricating hollow articles from blanks of the thermoplastic in which the thickness is small compared with the superficial area, so that maximum water up-take can be obtained in the course of a few days at the most, e. g. blanks in sheet-form or tubular form. Thus, for example, it is known to dish blanks of cellulose acetate sheet material by softening the blank by soaking in water, introducing it cold between heated male and female forming-members, and drawing the blank to the desired shape by bringing the forming members together.

It is also known to fabricate hollow articles, for example dolls, from cellulose acetate sheet material by soaking the material in water to soften it, inserting two of the softened sheets between a pair of mould-members which together furnish the cavity to which the article is to conform and introducing live steam between the sheets so as to blow them into the shape of a hollow article conforming to the mould cavity. In another method, used for instance in fabricating dummy-legs for demonstrating stockings, a tubular blank of cellulose acetate is softened by soaking in water and fixed in a suitably shaped split-mould, one of the open ends of the tube being closed by a plug, the mould is surrounded by hot water, and steam, hot water or air is forced into the other end of the tube to expand it and cause it to conform to the shape of the mould, after which the mould is cooled and opened and the moulding is removed.

In practicing such methods it has been found difficult always to obtain the desired sharpness of contour in the object produced, and also to avoid local irregularities in thickness and imperfections in surface. In seeking to avoid these difficulties I found that while considerable improvement could be obtained by appropriate formulation of the thermoplastic material and by careful control of the soaking period, attention to these factors did not always prevent the local irregularities in thickness and imperfections in surface referred to. These defects, however, I have found it possible to avoid by incorporating a wetting agent in the water used to soften the thermoplastic material.

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According therefore to the present invention, in a process in which a blank of an organic thermoplastic is softened by soaking in water and is formed into a predetermined shape by the application of heat and pressure to the blank while it still retains the absorbed water, a wetting agent is applied in conjunction with the water. The wetting agent need not be present in the soaking bath at the beginning. It appears to function by ensuring that the blank, when first subjected to heat in the shaping operation, shall carry on its surface a continuous film of water, and the wetting agent may therefore be applied at any stage such that this purpose is achieved. It may, for instance, be introduced into the soaking bath towards the end of the soaking period, or it may be absent from the soaking bath proper and the blank may be dipped immediately before shaping into a second bath containing a dilute solution of the wetting agent. The wetting agent should be applied in very low concentration, e. g. in the form of an aqueous solution containing 0.05 to 0.1% by weight of the wetting agent. The wetting agent may be used in the form of one or other of the commercial preparations comprising an aqueous solution of sodium secondary octadecyl sulphate together with small proportions of octadecyl alcohol and of salts such as sodium sulphate and sodium carbonate, the preparation being diluted to give a concentration of about 0.05 to 0.1% of the sodium octadecyl sulphate based on the weight of water.

The best results have been obtained by using anionic wetting agents, and especially the soluble salts, e. g., the sodium salts, of long chain alkyl sulphates and of aralkyl sulphonates. Apart from sodium secondary octadecyl sulphate, mention may be made of the di-octyl ester of sodium sulphosuccinic acid, of sodium alkyl naphthalene sulphonates, of sodium naphthalene sulphonate, Turkey red oil, and of triethanolamine oleate. Although anionic wetting agents are to be preferred, cationic wetting agent, e. g. cetyl pyridinium bromide, and non-ionic wetting agents, e. g. polyoxyalkylene ethers of sorbitan monolaurate, monopalmitate or mono-oleate, are also effective.

I have found that excellent results can be obtained by using for the material for the blanks, a cellulose acetate of the grade commonly used in transparent sheeting, plasticised with a mixture of a stiffening plasticiser, for example triphenylphosphate, with one or more softening plasticisers of high solvent power for the cellulose acetate, at least one of which has a substantial, but not

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large, solubility in water, for example a solubility of 3-10% and especially 3-5% by weight. A very suitable composition, for instance, is the following:

- 100 parts of a cellulose acetate containing 52 to 54% of combined acetic acid
- 35 parts of plasticiser of the composition:
 - 37 parts dimethylphthalate
 - 33 parts triphenylphosphate
 - 30 parts triacetin

all the parts being by weight.

Although the best results have been obtained with sheet material of the composition specified above, good results can also be obtained by replacing part or the whole of the various plasticisers by other plasticisers having similar properties. Thus, for example, the triacetin may be replaced by triethyl citrate and the whole or a part of the dimethyl phthalate may be replaced by diethyl phthalate or dimethoxy ethyl phthalate. The proportions of these plasticisers may also be varied to some extent; thus, for example, the proportion of the triphenylphosphate may be between 30% and 35% of the mixture of plasticisers and the triacetin may range from 28% to 35% of the mixture, the remainder being dimethyl phthalate, and the total amount of plasticiser may vary from 30% to 40% based on the weight of the cellulose acetate.

I have found that to obtain the best results the soaking of the sheet material in water before blowing must be carried out under carefully controlled conditions. Both the volume ratio of water to sheet material and the duration of immersion are important. Although the volume ratio of water to sheet material may be as high as 30:1 or even 100:1, with such high ratios the softening of the sheet is accompanied by undue leaching out of plasticiser, and I have found that considerably better results are obtained with much lower volume ratios, for instance between 8:1 and 12:1 and for the thinnest materials even lower, e. g. between 5:1 and 10:1. During immersion the absorption of water at first increases rapidly, after which there is a much more gradual increase. In estimating the total water absorption by increase in weight, loss of plasticiser by leaching out must of course be allowed for.

I have found it best to continue the immersion up to or but slightly beyond the point at which the rate of water absorption begins to fall off. In this way I have obtained high water absorption with relatively little loss of plasticiser.

The following examples illustrate the invention:

Example I

Cellulose acetate sheet material of thickness 0.030 in. formulated from a cellulose acetate containing 52 to 54% of combined acetic acid with a mixed plasticiser of dimethylphthalate, triphenyl phosphate and triacetin in the preferred proportions specified above, is soaked for 24 hours in 9 times its volume of water to which has been added 0.1% by weight of the wetting agent sold under the registered trade-mark "Teepol X," and comprising an aqueous solution containing about 20% of sodium secondary octadecyl sulphate, 6% of sodium sulphate and 4% of octadecyl alcohol.

This period of immersion results in an absorption of water amounting to about 85% of the amount that would be taken up if the immersion were continued for 12 days. The loss of plasti-

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ciser by leaching out, however, in this period is only 50% of the loss that occurs in 12 days.

The sheet material is removed from the soaking bath and two sheets are placed without drying between two mould halves, the cavities of which are shaped to form a doll's head. Steam is admitted between the sheets at a pressure of 40 lbs. per square inch. After 4 minutes the steam is shut off and the mould is cooled and opened.

Example II

The process is carried out as in Example I, but using sheet material of thickness 0.60 in. and soaking for 3 days.

Example III

The process is carried out as in Example I, but using sheet material of thickness 0.015 in. and soaking for 5 hours only.

In these examples the wetting agent used can be replaced by an equal weight of triethanolamine oleate. Blanks for the production of other hollow articles by the methods referred to above, i. e. by pressing cold in heated dies and by blowing with steam, hot water or air in a mould surrounded by hot water, can be made from material of the composition described, and softened as described in these examples.

The invention has been described with particular reference to the use of cellulose acetate sheet material. In a similar way, however, the principles outlined above can be applied in the fabrication of other organic thermoplastic materials, capable of being softened by soaking in water. Such materials are to be found, for instance among the thermoplastics having a basis of partial esters and ethers of cellulose, e. g. cellulose nitrate and ethyl cellulose, and especially those having a basis of a cellulose fatty-acid ester in which the ester groups contain 2 to 4 carbon atoms, e. g. cellulose propionate, cellulose acetate-propionate and cellulose acetate-butyrate. Naturally the cellulose ester or other high-polymer forming the basis of the thermoplastic must be of a suitable grade to give the desired mechanical properties in the products and must be capable of formulation to give a thermoplastic able to be softened by soaking in water. For this purpose the water absorption of the thermoplastic on soaking in water at 60° C. should preferably reach a maximum between 4 and 8% by weight. In obtaining the desired water-absorption in cellulose derivative thermoplastics, those derivatives having a degree of substitution between 2.25 and 2.75 are particularly useful. The use of cellulose derivatives of higher degree of substitution, e. g. cellulose acetates containing 55 to 62% of combined acetic acid, involves much greater difficulty in formulating to get the desired water-absorption.

Having described my invention, what I desire to secure by Letters Patent is:

1. Process for making hollow articles, which comprises softening a blank of material having a basis of an ester of cellulose in which the degree of substitution is between 2.25 and 2.75 and the ester groups of which contain 2 to 4 carbon atoms by soaking in water containing a wetting agent and heating the blank while it still carries a film of water on its surface and still contains the water absorbed during soaking, and forming the hot, softened blank into the desired hollow shape by the application of fluid pressure.

2. Process for blowing hollow articles, which comprises softening a blank of material having a

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basis of an ester of cellulose in which the degree of substitution is between 2.25 and 2.75 and the ester groups of which contain 2 to 4 carbon atoms by soaking the blank in water containing a cationic wetting agent and exposing one side of the blank to live steam under pressure while it still carries a film of water on its surface and still contains the water absorbed during soaking, and forming the blank into the desired hollow shape by means of said pressure.

3. Process for blowing hollow articles, which comprises softening a blank of thermoplastic material having a basis of cellulose acetate containing 52 to 54 per cent of combined acetic acid by soaking the blank in water containing a cationic wetting agent and exposing one side of it to live steam under pressure while it still carries a film of water on its surface and still contains the water absorbed during soaking, and forming it into the desired hollow shape by means of said pressure.

4. Process for blowing hollow articles, which comprises softening a blank of cellulose acetate containing 52 to 54 per cent of combined acetic acid and plasticized with 30 to 40 per cent of its weight of a mixture of triphenylphosphate, triacetin and dimethyl phthalate, by soaking the blank in water containing a cationic wetting agent until it has absorbed at least 85 per cent of the water it would absorb in 12 days' immersion but has lost no more than 50 per cent of the plasticizer it would lose in 12 days' immersion, removing the sheet, and forming it into the desired hollow shape under heat and pressure applied by exposing one surface to live steam under pressure.

5. Process for blowing hollow articles, which comprises softening a blank of cellulose acetate containing 52 to 54 per cent of combined acetic acid and plasticized with 30 to 40 per cent of its weight of a mixture of triphenylphosphate, triacetin and dimethyl phthalate, by soaking the blank in water containing sodium secondary oc-

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tadecyl sulphate until it has absorbed at least 85 per cent of the water it would absorb in 12 days' immersion, but has lost no more than 50 per cent of the plasticizer it would lose in 12 days' immersion, removing the sheet, and forming it into the desired hollow shape under heat and pressure applied by exposing one surface to live steam under pressure.

6. Process for blowing hollow articles, which comprises softening a blank of cellulose acetate containing 52 to 54 per cent of combined acetic acid and plasticized with 30 to 40 per cent of its weight of a mixture of triphenylphosphate, triacetin and dimethyl phthalate, by soaking the blank in water containing triethanolamine oleate until it has absorbed at least 85 per cent of the water it would absorb in 12 days' immersion, but has lost no more than 50 per cent of the plasticizer it would lose in 12 days' immersion, removing the sheet, and forming it into the desired hollow shape under heat and pressure applied by exposing one surface to live steam under pressure.

7. Process according to claim 4, wherein the hollow article is blown from two sheets of the wet blank by means of steam introduced between two mould-members which together provide the cavity to which the blown article is to conform.

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