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PRODUCTION OF HOLLOW PRODUCTS

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Fig. 1

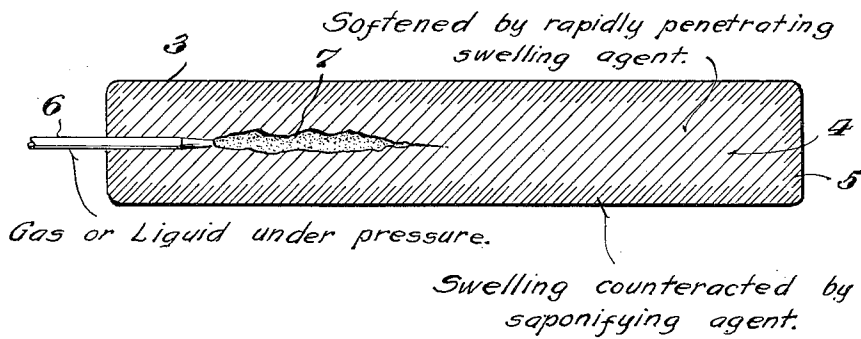
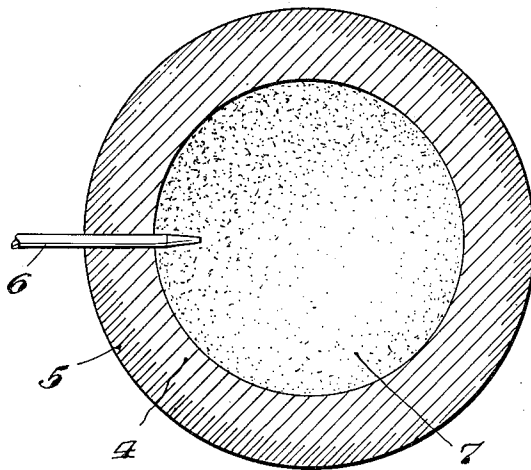


Fig. 2



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PRODUCTION OF HOLLOW PRODUCTS

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10 Claims. (Cl. 18—47.5)

The invention concerns the production of hollow products of every kind, especially cylindrical, conical, ball-shaped, bladder-shaped and ellipsoidal hollow shaped products from sheets shaped accordingly, from cellulose derivatives.

It has already been proposed to produce hollow shaped cellulose products by treating a jelly-like skin of viscose, i. e., a strongly alkaline film of cellulose xanthogenate, first with a solution of sodium chloride, and then with a solution of zinc sulfate, zinc chloride, lead acetate or tin dichloride. During this treatment the skin is supposed to part in two or split in two lengthways, while the edges remain joined. The skin thus doubled is blown up by inner pressure of a liquid injected into it, whereby a hollow product is obtained. This process, however, cannot be carried out, at least not in case undamaged hollow shaped products are wanted, because neither starting material nor treating agent are suited for carrying this process into effect.

According to the present invention it has been found that hollow shaped products can easily be produced from sheets suitably shaped, for example cylindrical hollow products from ribbon-shaped sheets or ball-shaped hollow products from circular sheets, by using as starting material sheets of organic cellulose esters or ethers or of nitrocellulose, that is of cellulose derivatives free from sulphur, by subjecting these sheets to partial saponification and simultaneous swelling. By this treatment the strength of the sheets is reduced from the outside towards the inside, or vice versa is increased from the inside towards the outside. Therefore the bodies thus treated may by mechanical treatment be split up and hollowed out at the spot which is least resistant. Thus a hollow shaped product is obtained.

For the production of hollow shaped products sheets of organic cellulose esters, for example cellulose acetate, formate, propionate, butyrate, tolylsulfonate, or nitrocellulose, or mixed esters, for example nitroformate or butyryl acetate, or cellulose ethers, for example methyl, ethyl or benzyl cellulose are employed.

Preferably such sheets of cellulose esters are employed, which have been admixed with softening agents, especially phthalic acid, for example diethyl, dibutyl or dimethylglycol phthalate as they are known under the trade-mark "Palatinol A, C or O," furthermore castor oil, paraffin oil, triphenyl or tricresyl phosphate.

In carrying out the invention the sheets, which form the cross section of the tri-dimensional de-

sired product (for example for the production of tubes, a ribbon-like shape) are subjected to partial saponification and simultaneous swelling, by which treatment their strength is reduced from the outside towards the inside, or increased from the inside towards the outside. Their strength may be diminished or their compactness be changed to the extent that the material dissolves in the treating agent or in a constituent thereof. The treating agent affects equally both of the frontal sides as well as the edges of the sheet and penetrates towards the centre of the sheet.

As treating agent a mixture of saponifying agent and swelling agent is used. According to the kind of starting material basic agents, for example sodium hydroxide, potassium hydroxide, soda lye, milk of lime, ammonia, amines or strong acids, for example sulphuric acid, hydrochloric acid or nitric acid are used. As swelling agents in almost all cases alcohols, such as methyl, ethyl or isopropyl alcohol may be employed. Solvents may be used for the sheet-substance as well, provided that their solvent effect is suppressed by a non-solvent to such an extent that only a swelling effect takes place. For swelling primary cellulose triacetate the following swelling agents or solvents are suitable: glacial acetic acid, chloroform or methylenechloride. For swelling secondary cellulose triacetate the following swelling agents or solvents are suitable: methylenechloride, acetone, methyl ethyl ketone, dioxane, benzyl alcohol, cyclo hexanone, methyl glycol and diacetone alcohol. For swelling cellulose nitrate acetone or other ketones or mixtures of alcohol and ether are suitable. For swelling formyl cellulose pyridine, formic acid, furfural, glycol or ethylenechlorhydrine are suitable. In almost all cases hydrocarbons, such as benzene, toluene or xylene or water may be used as non-solvents. The solvent effect of some of the solvents may be suppressed by alcohols which have swelling qualities. When sheets of cellulose triacetate are used carbon tetrachloride as well as ethers, for example diethyl, dipropyl or butylamyl ether may be employed. When sheets of formyl cellulose are employed the effect of the solvent may be suppressed by the addition of acetone.

In some cases one does not succeed in producing a homogenous mixture of the saponifying agent, the swelling agent and any non-solvent used. In such cases a further solvent may be added, which has a homogenizing effect on the mixture. For example in a mixture of sodium hydroxide as swelling agent, methylene chloride

as solvent and ethyl alcohol as non-solvent, which mixture is suitable for treating sheets of cellulose triacetate, sodium hydroxide separates out. If, however, methyl alcohol is added to this mixture, a homogenous mixture is obtained, which does not separate into layers.

When treating a sheet with such a mixture of saponifying agent and of swelling agent or saponifying agent, solvent and non-solvent, if desired with the addition of a homogenizing agent, the swelling agent or solvent respectively penetrates from the surface to the core of the sheet with a certain velocity, whilst the saponifying agent or the non-solvent, which suppresses the dissolving effect of the solvent, or both of them, diffuse into the sheet with less rapidity. Sheets are obtained, which in their inner part are swollen or even dissolved to a far reaching extent by the swelling agents or the solvents respectively, while the strength of the edges, or, in other words, of the whole surface, is only slightly changed or even increased by the action of the saponifying agent or the non-solvent respectively. Usually there is not an abrupt but a very gradual transition from the inside towards the outside.

This treatment being concluded it is very easy to split up the sheet at its least resistant spot, that is according to its shape either in the centre or along its axis or around a central plane. Thus a hollow shaped product is obtained. This may easily be effected by mechanical methods, such as rubbing or shoving one surface against the other, for example holding the sheet-like product between thumb and forefinger and then letting ones thumb pass over ones forefinger, or treating it between squeezing rollers or in a wringing-machine and passing liquid or gas through the product. Another method consists in bulging out the treated sheet by passing through liquids or blowing it up by gases. There are two embodiments of the last method. Either liquid or gas are injected into the treated sheet from the outside, or gases are produced in the inside of the sheet, for example by adding a liquid which boils at low temperatures, to the treating agent. This liquid penetrates into the inner part of the sheet and evaporates when the sheet is heated.

In many cases the hollow shaped products are, if desired after drying, ready for use. In some cases the insides of the bulged out shaped product tend to stick together and combine again. This tendency must be avoided by drying or rinsing, in order to destroy or wash out the sticky substance.

The hollow shaped products according to the invention may serve for various purposes according to their shape and to the kind of material they are produced from. Thus tubes are obtained from ribbon-like sheets, which may for example, according to the starting material, be used as fuel piping or artificial sausage skin. From circular or round sheets bladder-shaped hollow products are obtained, which may serve as hog bladder substitutes or balloons. Furthermore a great variety of seamless bags of every kind, which, for example may be made use of in the food industry, may be produced. There are of course, many other products, such as finger-stalls, gloves and so on, which can be produced in the afore-described way.

As illustrating the novel process, I have shown a typical procedure in the accompanying drawing in which

Fig. 1 shows a vertical section of a sheet undergoing treatment and

Fig. 2 shows the final stage of development.

In the drawing, the sheet 3 is illustrated as having its composition softened throughout and substantially uniformly with a rapidly penetrating swelling agent. Simultaneously with this action the more slowly penetrating saponifying agent restores the strength of the surface. Thus the main body 4 is softened and the outer or superficial area 5 has the softening suppressed or counteracted. If then a hollow needle 6 or equivalent device is inserted and a gas or liquid introduced under pressure, the inner portion will divide to provide a cavity 7.

Any desired hollow form may be given and Fig. 2, shows distending the sheet into a sphere.

Examples

(1) Ribbons, cut from a sheet which is 0.05 mm. thick of secondary cellulose triacetate, are submerged in a bath which consists of 5 volumes of an aqueous solution of 30% sodium hydroxide, 55 volumes of methylene chloride, 20 volumes of ethyl alcohol and 20 volumes of methyl alcohol, for 5 minutes. During this treatment the following reactions take place:

The methylene chloride, which has a swelling effect on the cellulose triacetate penetrates rapidly from the surface and the edges of the cellulose triacetate ribbon into its centre (inner part). The ethyl alcohol, which represses the dissolving effect of the methylene chloride, diffuses into the sheet with less rapidity. The sodium hydroxide solution, which serves as saponifying agent, penetrates still more slowly. At the end of the treatment the sheet consists in its central inside of unsaponified or almost unsaponified cellulose triacetate, which has been swollen in methylene chloride, or even a solution of cellulose triacetate in methylene chloride. The layers lying between centre and surface consist of cellulose triacetate which is swollen to a minor degree because saponified to a higher degree. Finally the sheet's facial layers consist of cellulose triacetate which has been saponified to a still higher degree and are therefore only slightly swollen. The strength of the treated sheet diminishes gradually from the outside towards the inside, the inner part representing even a solution of cellulose triacetate in methylene chloride. If for example such a sheet is thrown into a water bath, the temperature of which lies above the boiling point of the methylene chloride, the methylene chloride within the swollen sheet evaporates and blows up the ribbon-like sheet into a cylindrical or ellipsoidal product respectively.

For hollowing out the sheet another method may be used, by which it is treated between squeezing rollers or is cut open at one end, and a jet of water is led into and passed through the opened sheet. By another embodiment the sheet is brought into a room heated to a temperature which lies above the boiling point of methylene chloride. A tube-like product is obtained, which may, for example, serve as artificial sausage skin.

(2) Sheet products shaped like a bladder which is pressed together are cut out of a sheet of cellulose triacetate. These shaped products are treated in a rotating fulling tub for 3 minutes with a mixture, which consists of 20 volumes of an aqueous solution of sodium hydroxide of 30%, 40 volumes of methylene chloride, 30 volumes ethanol and 10 volumes methanol. Hereafter

this bath is led away from the fulling tub, which is filled again with hot water. If the sheet products are inflated they take the shape of artificial bladders. When cooling down they collapse again. They may, however, be blown up again at any time, and be used as containers for meat products.

(3) Rectangular cuttings of a sheet of cellulose nitrate are treated in a bath consisting of 66 parts of a mixture of 5 parts of alcohol with 3 parts of ether, 34 parts of Palatinol and 10 parts of an aqueous solution of sodium sulfide for 2 minutes. The mixture of alcohol and ether selected for the purpose has a strong swelling effect on the cellulose nitrate and penetrates into the sheet very rapidly. The softener, on the contrary, not only reduces this swelling but even prevents it and diffuses rather slowly into the sheet. Finally the sodium sulfide splits off the nitro groups. The result is a sheet with a highly swollen or even dissolved core, which is surrounded by a number of layers, which according to their position, are progressively more denitrated and therefore progressively less swollen. After this treatment the swollen rectangular sections are brought into a stream of hot air, in which they are blown up and form a bag-like product. The bags may be cut open on one side and closed by gluing or some other arrangement. They may be used as bags for explosives.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

1. A process for the production of hollow shaped products from saponifiable thermoplastic cellulose compounds free from sulphur, which comprises treating sheets of such compounds of suitable shape with an agent which reduces the strength of the sheet products from the inside towards the outside, said agent comprising a mixture of at least one saponifying agent and at least one swelling agent for the cellulose compound, thereby producing an article which, from the outside towards the inside, is saponified in a progressively lesser degree and therefore swollen and weakened in a progressively greater

degree, splitting such article in the interior most weakened portion thereof, and separating the surfaces formed by such splitting to form a hollow body.

5 2. Process according to claim 1, wherein the separating of the surfaces is effected by cutting open the sheet at one point and passing a gas therethrough.

10 3. Process according to claim 1, wherein the splitting is effected by rubbing one side of the article against the other, and the separating is effected by cutting open the sheet at one point and passing therethrough an agent selected from the group consisting of liquids and gases.

15 4. Process according to claim 1, wherein sheets of organic cellulose esters are treated.

5. Process according to claim 1, wherein basic agents are used as saponifying agents.

20 6. Process according to claim 1, wherein a mixture of a solvent, with a nonsolvent which diminishes the dissolving effect of the solvent, is employed as swelling agent.

25 7. Process according to claim 1, wherein the mixture of saponifying agent with swelling agent is so chosen that the inside of the sheet dissolves in the swelling agent.

8. Process according to claim 1, wherein the split products are freed from substances which may cause the insides to stick together.

30 9. Process for the production of hollow shaped bodies, which comprises treating a sheet of cellulose triacetate of suitable shape with a mixture of aqueous solutions of an alkali hydroxide, a chlorinated hydrocarbon, and at least one alcohol, thereby producing an article which, from the outside towards the inside is saponified in a progressively lesser degree and therefore swollen and weakened in a progressively greater degree, splitting such article in the interior most weakened portion thereof, and separating the surfaces formed by such splitting to form a hollow body.

40 10. Process according to claim 9, wherein the sheet of cellulose triacetate is treated with a mixture of aqueous sodium hydroxide, methylene chloride, ethyl alcohol and methyl alcohol.

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