Cl. 15

Published Apr. 27, 1943

Serial No. 326,533

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF HOLLOW PRODUCTS

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No Drawing. Application filed March 28, 1940

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 strong alkaline film from cellulose xanthogenate, to begin with 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 a combined whole. 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 shaped accordingly, for example cylindrical hollow products from ribbon-shaped sheets or ball-shaped hollow products from circular sheets, by using as starting material sheets from organic cellulose esters or ethers or from nitro cellulose, that is from cellulose derivatives free from sulphur, and in subjecting these sheets to partial saponification and simultaneous swelling. By this treatment on the one hand the sheets' strength is reduced from the outside towards the inside, or vice versa is increased from the inside towards the outside. Therefore the so treated bodies may by mechanical treatment be opened at the spot which is least resistant. Thus a hollow shaped product is obtained.

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

Preferably such sheets from 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 somehow represent a cross section of the tridimensional desired product, which, for example during the production of tubes represent a ribbon-like sheet, 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 such an extent that it dissolves in the treating agent or in a constituent thereof. The treating agent is equally affecting both of the frontal sides as well as the edges of the sheet and is penetrating 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 effect of solving 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 methylene chloride. For swelling secondary cellulose triacetate the following swelling agents or solvents are suitable: methylene chloride, acetone, methyl ethyl ketone, dioxane, benzyl alcohol, cyclo hexanon, methyl glycol and diacetone alcohol. For swelling cellulose nitrate acetone or other ketones or mixtures from alcohol and ether are suitable. For swelling formyl cellulose, pyridine, formic acid, furfurol, 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 solving effect of some of the solvents may be suppressed by alcohols which have swelling qualities. Sheets from cellulose triacetate being used carbon tetrachloride as well as ethers, for example diethyl, dipropyl or butylamyl ether may be employed. Sheets from formyl cellulose being 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 if desired, a non-solvent. In such cases a further solvent may be added, which has a homogenising effect on the mixture. For example in a mixture of sodium hydroxyde as swelling agent, methylene chloride as solvent and ethyl alcohol as non solvent, which mixture is suitable for treating sheets from cellulose triacetate, sodium hydroxyde sedates. 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 swelling agent or saponifying agent, solvent and non-solvent, if desired with the addition of a homogenising agent, the

swelling agent or solvent respectively is penetrating from the surface to the core of the sheet with a certain velocity, whilst the saponifying agent or the non-solvent, which suppresses the solving effect of the solvent or both of them are diffusing into the sheet with less rapidity. Sheets are obtained, which in their inner part are swollen or even solved 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 help 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 pass one's thumb over one's forefinger, or treating it between squeezing rollers or a wringing-machine. 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 liquid which is boiling 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 bladders 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, still many products, such as finger-stalls, gloves and so on, which can be produced in the aforedescribed way.

Examples

(1.) Ribbons, cut from a sheet which is 5 mm strong, from secondary cellulose triacetate, are submerged into 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 is penetrating rapidly from the surface and the edges of the cellulose triacetate ribbon into its centre (inner part). The ethyl alcohol, which is suppressing the solving effect of the methylene chloride to a far reaching extent, diffuses into the sheet with less rapidity. The sodium hydroxide solution, which serves as saponifying agent, is penetrating still slower. At the end of the treatment the sheet, which is now highly swollen, consists in its central inside of non or almost non saponified 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 lesser degree but saponified to a higher degree. Finally the sheet's surfacial layers consist of cellulose triacetate which has been saponified to a still higher degree and is only slightly swollen. The strength of the treated sheet is diminishing gradually from the outside towards the inside, the inner part representing even a solution of cellulose triacetate in methylene chloride. If, by experiment, 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, into which a jet of water is lead and passed through the 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 received, which may, for example, serve as artificial sausage skin.

(2.) Sheet products shaped like a tub which is pressed together (tub=German "Butte" or "Bütte") are cut out of a sheet from 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 hydroxyde 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. The tubs are inflated and represent artificial tubs. 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 sections of a sheet from 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, does not only reduce 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 solved core, which is surrounded by a number of layers, which according to their position, are still less swollen and still more dinitrated. After this treatment the swollen rectangular sections are brought into a steam of hot air, in which they are blown up and represent 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.

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