

# ALIEN PROPERTY CUSTODIAN

## MANUFACTURE OF ARTIFICIAL FIBRES, THREADS, BANDS, RIBBONS, HORSEHAIR, FILMS AND THE LIKE

Leo Ubbelohde, Berlin-Charlottenburg, Germany; vested in the Alien Property Custodian

No Drawing. Application filed January 22, 1941

The present invention relates to an improvement of artificial fibres, films, threads, ribbons and the like, more especially to an improvement of these products which have been treated with artificial resins, as, for example, condensation products of phenols and aldehydes.

It has already been proposed to improve the dyeing quality of artificial structures, such as textile fibres, for example, made from cellulose or cellulose derivatives, by treating them with condensation products of phenols and aldehydes. But the fibres treated by this method always showed a change in colour increasing step by step and turned to a yellowish or brownish colour after a certain time. When performing this method resoles had been used which were manufactured according to the presumed formation of phenol resins, according to which firstly oxydarylmethane is formed in the usual way from phenol and aldehyde in a molecular proportion of 1 mol of phenol: 1-1.3 mols aldehyde in adding alkaline condensation agents.

Now it has been found that the structures treated with these substances, for example, textile fibres or films made of cellulose or cellulose derivatives or of other synthetic substances turn to yellow, and that this turning to yellow is caused by the method of condensation of the resoles used, that is to say of the resoles in which free phenols are still present and further the resoles consisting of very low molecular condensation products of phenol and formaldehyde. Such products may also only be formed afterwards from the resoles used for the treatment.

Further on, it has been found that these faults can be eliminated, that is to say that artificial fibres, threads, films and the like may be improved without the danger of a turning to yellow when using resoles which are manufactured in the following manner:

The equilibrium of the reaction is moved in disfavour of the phenols; if, for example, 1 mol phenol is condensed in the presence of substantial quantities of strong alkaline condensation agents, as, for example, NaOH, NaHCO<sub>3</sub>, Na-phenolate and the like with more aldehyde as usual, that is to say with more than 1.3 mols formaldehyde, suitably with more than 1.5 or 2 mols, for example, with 3 mols and more formaldehyde, and if the resulting resole is added to the spinning solution for spinning artificial fibres, these fibres will show extremely good qualities afterwards, especially they will no more turn to yellow.

When performing the condensation reaction as set forth heretofore, very high molecular resoles

will result, which nevertheless will have a sufficient solubility in alkaline lye and the quality of such resoles will, which is most surprising, not be changed or destroyed by the alkaline spinning solution of cellulose and by solutions of cellulose derivatives, for example, of cellulose ethers or esters, nor by other solutions, which are used for manufacturing artificial structures, so that, for example, viscose, which is mixed with this resole may be spun in the usual way in using an acid coagulating bath or even in using water or air as a coagulating medium, and, in the last two cases, acidulating the formed structures. Afterwards the resole will be precipitated from alkaline solution by the contact with acid spinning baths and will begin to solidify and to harden under the influence of the acid, that is to say will go over into a resitol or a resit.

The presence of cellulose will, which is most surprising, not hinder the hardening, but it hinders that the hardening of the resin condensed with much formaldehyde will go on too quickly, which otherwise will be the case when a contact with sulphuric acid, for example, of the acid-precipitating bath, working as a catalysator, takes place. Therefore it is, for example, possible to crinkle or undulate the threads in a known manner, for example, by shrinking or crinkling them in a chemical or mechanical way before the resin has become hard and lost its plasticity.

Further, it is possible thoroughly to perform the hardening, after having washed out the acid, by drying the threads or by applying heat to the artificial structure, for example, by heating them to 90 or 100°C or more. If an unimportant turning to yellow still should come forward this may be neutralized by mixing substances, as, for example, titanium dioxide to the spinning solution. The dyeability of the formed structures may be increased by working urea or its derivatives or sulphur compounds into the resoles, for example, by treating the resoles with a chloride of sulphur or the like, whereby the chloride of sulphur or the like may be dissolved in an organic solvent.

According to the present invention fibres, threads, ribbons, films or the like may be manufactured, which show especially good qualities and which will not show a discolouring and keep a great strength and besides keep the form given to them, for example, a crinkled or undulated form or the like.

### Example

A viscose of usual composition is mixed with

2 per cent or more or less of a previously condensed mixture (resole), consisting of 1 part of wet crystalline phenol and 3 parts of wet formaldehyde (37-40 volume-per-cent), which is condensed in using an aqueous solution of  $\text{NaHCO}_3$  or  $\text{NaOH}$  as a catalysator. The condensation, respectively polymerization, which takes place under the influence of heat, for example, at the boiling temperature and under the influence of the alkali is prosecuted until the formed resole shows a proper consistence, but it may also be broken off in an earlier state, at which the product is still easily soluble in alkaline solutions, by adding a small surplus of acid. In this case the boiling is continued and the evaporated aldehyde is exhausted by suction. As soon as the composition has got the proper consistence it is quickly cooled down to  $100^\circ\text{C}$ , so that no further change takes place, and afterwards cooled down further either quickly or slowly.

The resulting product is soluble in water and in alkaline solutions, as, for example, in aqueous  $\text{NaOH}$  and is dissolved to a concentration of about

8% and added to the viscose, and the mixture is spun to threads or the like using an acid coagulation bath in usual manner. When leaving the coagulating bath the coagulated threads may be crinkled and after the acid has acted a sufficient long time, the structure is washed and afterwards treated and dried at a temperature sufficiently high, for example, of  $80^\circ$  or more, that is to say about  $100^\circ\text{C}$ . The more resole is added to the spinning solution the more the effect described will be produced. It is possible even to add 10 or 20% or more resole to the spinning solution.

The Example described herebefore is only to be looked at as one way of performing the invention, other ways are possible, for example, in changing the character of the spinning solution to be used, for example, in using cellulose-esters or -ethers or casein solutions or mixtures of these substances, or the constitution of the resole added to it, as set forth in the description given hereinbefore.

LEO UBRELOHDE: