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Protein - acrylate graft copolymers for leather finishing

The finishing of leather is an age old process but it is the least understood phase of the leather industry. The reason for this is probably that the finishing of leather has long been more of an art than a science. The requirements of leather finishes are much more varied and complicated than most other applications of coating. The substrate differs from one type of leather to another and the requirements with regard to flexibility, adhesion, abrasion resistance, fastness to light etc. are very high. The leather finishing is a fast changing industry dictated by the ever changing fashion trend, the ever increasing demand of quality and the availability of new polymeric materials. It is necessary to emphasise that the most important task is to make leather handsome, serviceable and desirable by using modern finishing polymeric materials such that it will be able to stay ahead of leather substitutes. Different polymeric finishing materials both natural and synthetic are used in the present day leather industry. Among the natural high polymeric materials widely used for finishing leather are casein, shellac, waxes, egg and blood albumin, water soluble gums, rubber latex, glue and gelatin. With the development of synthetic high polymers and the inherent disadvantages of natural polymers, the application of protein finishes in the leather field has been offset to a greater extent. However, attempts have been made¹⁻³ in recent years to graft casein, gelatin and other inedible proteins with vinyl polymers and these products have been tried as binders and leather dressing materials. In this note, we report the work carried out in our laboratory to develop new binders, impregnating agents, leather dress-

ing materials and other tanning aids based on collagen dissolution products and tannery waste products and other biopolymers. Various graft copolymers with different types of backbones such as gelatine, glue, casein, and hide fleshings and vinyl side chains have been prepared and evaluated in leather processing.

The choice of monomers and initiatory systems is particularly significant since it has the major influence on many of the desirable properties of the grafted products. To obtain the most desirable properties of the grafted branch polymers, two or more monomers have been polymerised to form graft copolymers on the backbones.

Experimental

Materials

Gelatine, glue and casein were all commercial grade. Undistilled vinyl monomers obtained from Rohm and Haas were used without further purification.

Hide fleshings

Hide fleshings were first treated with boiling water to remove the fats. This solution was filtered off and the residue was treated with pepsin at PH2 for two days. The dissolved products were taken for grafting experiments.

Grafting procedure

The following procedure gives the method of preparation of a representative sample. An aqueous solution of the protenaceous products, the monomers and persulfate (potassium or ammonium) was stirred at room temperature and the mixture was heated to 60-80°C until polymerisation was complete (1 hr). Other initiating systems such as redox systems and peroxides have also been used depending upon the back-

bone substrate and the end use of the product. In the case of casein, esters of acrylic and methacrylic acids were polymerized with previously solubilised casein in triethanolamine or borax. For the sparingly water soluble monomers aqueous emulsion technique has been followed.

Results and discussion

Stable, homogeneous and opalescent solutions with unlimited miscibility in water were obtained in all the cases of grafted samples. However, the monomer protein ratio was found to be highly significant. More of the protein gave coagulated products in some cases. Higher temperatures quickened the rate of reaction. Films with varying elasticity, hardness and resistance were obtained by using different monomers and their combinations and also by varying their proportions. Grafted samples have been evaluated for application on different types of leathers. Preliminary results obtained indicate that these can be suitably utilised as binders, impregnating agents and dressing materials for leather. Film performance of these modified proteins was better and also more economical than nitrocellulose lacquers for finishing of leather. Further work is in progress to find the specific type of product for a special application on to leather. Attempts are also being made to modify nitro-cellulose and cellulose acetates by graft copolymerization with vinyl polymers

with a view to improve their film-forming characteristics.

Santappa *et al.*⁶ have recently prepared and characterised a number of graft copolymers of chlorinated rubber and vinyl monomers. Rubber latex and chlorinated rubber have been used for finishing of certain types of leathers. In view of certain disadvantages of these materials, attempts are being made to prepare graft copolymers of rubber latex and chlorinated rubber with different vinyl monomers and evaluate them in leather finishing applications. The results will be published elsewhere.

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