Reprinted from the *Journal of Scientific & Industrial Research*, Vol. 33, May 1974, pages 243-257

Polymers & Their Role in Leather Science

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POLYMER science is one of the most active and promising fields in science, covering a multitude of topics from natural polymers that are of utmost importance for living systems to inorganic macromolecules. Recent years have seen a series of astonishing advances in the field of polymer science. The intensive activity in the field of polymer research, of course, has been a reflection of their widespread application in industry and domestic life. Synthetic polymers have assumed a significant role in man's economy in numerous forms, such as plastics, resins, rubbers, films, fibres, impregnants, surface coating materials, and finishing agents. The progress of an applied science, such as leather chemistry is, as a matter of course, dependent upon general advances of the fundamental sciences. The leather industry has been profoundly influenced by major discoveries in the field of polymers. Today it is very clear that many of the basic materials used by the leather industry are the result of research by polymer chemists. Collagen is also basically a high polymer composed of amino acids linked together by peptide bonds.

The literature on the role of polymers in leather science is obviously too vast to be covered in its entirety in this review. We shall draw attention here to specific areas in which substantial advances have been made. To keep the size of this article within reasonable bounds, we shall not go into the details of the preparation and physico-chemical properties of the polymers and their constituents. Comprehensive coverage of these aspects has been made in a number of recent books[1-40], reviews[41-48] and symposia proceedings[49-51]. Our deliberate bias, throughout this review, will be towards the application of polymers in leather manufacture rather than towards the fundamental chemistry. Although a few surveys of a limited scope have appeared[52-62] in recent years, no comprehensive survey of the role of polymers in leather science has appeared. The primary purpose of summarizing many of the applications of polymers in leather manufacture is to demonstrate that polymers have

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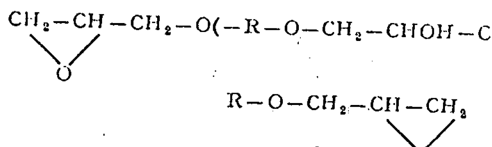
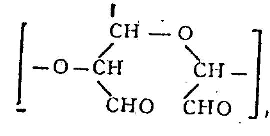
TABLE 1 — SOME IMPORTANT TYPICAL POLYMERS USED IN LEATHER INDUSTRY

Name of the polymer	Formula
Polyacrylates	$\left[-CH_2-\underset{CO_2R}{\underset{\vert}{CH}}-\right]_n$
Polymethacrylates	$\left[-CH_2-\overset{CH_3}{\overset{\vert}{\underset{CO_2R}{\underset{\vert}{C}}}}-\right]_n$
Polyurethanes	$\left[-O-R-O-\overset{O}{\overset{\Vert}{C}}-NH-R'-NH-\overset{O}{\overset{\Vert}{C}}\right]_n$
Polysiloxanes	$\left[-\overset{R}{\overset{\vert}{\underset{R}{\underset{\vert}{Si}}}}-O-\right]_n$
Poly(vinyl acetate)	$\left[-CH_2-\underset{O-COCH_3}{\underset{\vert}{CH}}-\right]_n$
Poly(vinyl alcohol)	$\left[-CH_2-\underset{OH}{\underset{\vert}{CH}}-\right]_n$
Rubber (Polyisoprene)	$\left[-CH_2-\underset{CH_3}{\underset{\vert}{C}}=CH-CH_2-\right]_n$
Polysulphides	$(-R-S-S-R-)_n$
Polyepoxides	
Dialdehyde starch	
Polyamides	$H-[-NH-R-Co-]_n$
Polyureas	$\left[-\underset{O}{\underset{\Vert}{C}}-NH-(CH_2)_x-NH\underset{O}{\underset{\Vert}{C}}NH(CH_2)_y-NH-\right]_n$

already made significant contributions in leather manufacture and that potential uses extend to almost every step (from soaking to finishing) in the conversion of hides to leather. In Table 1 are listed some of the important typical polymers used in the leather industry.

Polymers as Leather Impregnants

Impregnants and finishes are the major fields of application of polymers, both natural and synthetic, in leather technology. Finishes are restricted to the surface regions, while impregnants are allowed to penetrate deeper into the substrate. Materials like rubber, acrylics, silicones and polyurethanes have been used to fill the voids in leather. The main objective is to impart to leather water resistance with improved uniformity in quality of leather. The deleterious effect of water on leather is well known. When wet leather is allowed to dry, it usually becomes stiff and uncomfortable. Other objectives relating to the process of impregnation are the whitening of chrome tanned leather by deposition of resins, the making of leather substitutes by the bonding of aggregates of leather fibres and the increase in the abrasive resistance, break and scuff resistance of leather. The principal polymeric products used in leather industry as impregnants covering their main advantages and disadvantages with their basic chemistry in brief are given below.

Acrylates and Acrylic Emulsions as Leather Impregnants

Acrylate and methacrylate esters are derivatives of the corresponding acids[1,6-9,41]. The respective structures are:

$$CH_2=CHCOOR$$
$$CH_2=C(CH_3)COOR$$

The principal commercial routes to the lower acrylates are now based on ethylene cyanohydrin[63], acetylene[64] or β-pripiolactone[65]. Methacrylates are mainly produced by the acetone cyanohydrin process[34,66] and by the oxidation of isobutylene[67].

The earliest use[68] of acrylic polymer dispersions was in finishing of leather as base coats for nitrocellulose finishes and as components of water finish systems. The main principles of resin impregnation of leather were disclosed by Lawler[69]. Buechler *et al.*[70,72] discussed the process of aqueous impregnation and these authors have shown that impregnation with the preformed polymers improves the break scuff resistance and cutting value of the treated leathers. The location and effects produced by various types of preformed polymers, with particular reference to the histological variations of leather were also investigated by them[72]. Brown *et al.*[73] analysed the effects of surface tension on the speed of penetration of impregnants. Aqueous acrylic impregnation was also discussed by Quinn[74], Shaw[75], Merken *et al.*[76], Christensen[77], Brueter[78] and Rieger[79] and it is also covered in the patents of Lowell *et al.*[80] and Mattei *et al.*[81,82]. Grief[83] and Dolnick[84] studied the different aspects of aqueous as well as solvent based impregnations. These treatments are applied[85] by various methods, such as spray and curtain coaters, seasoning, machine and dip to leather at different stages. However, there are no generally accepted standards of application. One has to choose the specific type of impregnation for the type of leather he produces, since the process of impregnation is influenced by the previous retanning and fatliquoring processes.

The behaviour of leather when adding polymer impregnation agents and the advantages or unfavourable effects on the quality of the grain tightened leather were outlined by May[86]. The use of grain impregnation methods in practice and the influence of added quantities of the impregnant as well as the different methods of treatment on the properties of finished leather were also discussed by him. Penetration and binding mechanisms are explained as a function of surface charge, surface tension and concentration of the polymeric agent. Swelling and plumping of leather fibres show a decisive importance. The technique of grain impregnation to improve the inferior raw hides for the manufacture of shoe upper leathers and detailed working procedures were discussed by Schiffers[87]. The technique of applying the impregnants by various methods and tools and the influence of drying process on the efficiency of impregnation were also dealt with. Leather used in shoe soles requires a high abrasion resistance and the internal deposition of polymer can markedly improve this property. Donath[88] compared the polyurethane and acrylic leather impregnation system from the theoretical and practical viewpoints, details of which are given under the head 'Polyurethanes'.

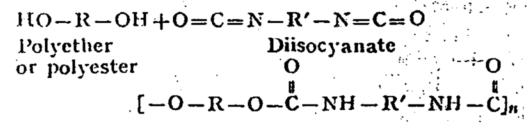
Zurabjan[89] studied the mechanical properties of leather and the changes in its macrostructure after treatment with polymers. The method of treatment and the properties of the polymer determine the nature of the copolymer. It is most important to note that the polymer treatment does not cause undue hardness of the leather or substantially reduce its water vapour permeability and water absorbing capacity. The ability of the polymer to form a film has a strong bearing on the mechanical properties of the copolymer. The adhesion power between the added polymer and collagen also strongly influences the mechanical properties of the copolymer.

Recently, a great deal of work has been done[90,91] on drum impregnation using acrylic polymers. This is a new approach of impregnation as compared to aqueous table impregnation. Arbaud[91] described the advantages of drum impregnation of light leathers with acrylic retanning resins in preference to table impregnation. A new product based on a nonpolar resin made water-soluble by adding carboxylic groups, which could be used for drum impregnation of sheep skins was described. Recently, attempts have been made to modify long chain fatty acids with acrylics for using them as fatliquoring and filling agents for leather.

Acrylic polymers used for impregnation have certain essential properties, viz. they are soft and have low particle size. Softness is an essential requirement, because too hard polymers would impair the temper of the leather. Low particle size is important, because relatively large particle size polymers are not able to penetrate into the grain layer of the leather. The most important effect of acrylic impregantion is that it greatly impoves the break of leather. The impregnated leather is well sealed, so that the subsequent finish coats can stay on the surface and a well-filled smooth, appearance results. An additional benefit is that quite often there is an improvement in the scuff resistance of the leather. The leather manufacturer can select a great number of acrylic monomers for the preparation of polymers, so that he can tailor-make the particular polymer for each special end use.

Polyurethanes

Polyurethanes[11-13,42], also referred to as 'urethanes or isocyanate polymers', have been for the last few years among the fastest growing segments of the polymer industries. Polyurethanes are characterized by the linkage $-NH-\overset{\displaystyle O}{\overset{\|}{C}}-O-$ (urethane), although other groups, such as ether, ester, biuret, allophnate, amide, etc., may be present in the polymer molecule. There are different methods for the preparation of polyurethanes, but the most widely used one is the reaction of di- or polyfunctional hydroxyl compounds, such as hydroxyl terminated polyethers or polyesters with di- or polyfunctional isocyanates. Difunctional reactants give linear polymers, as shown schematically below:


$$HO-R-OH + O=C=N-R'-N=C=O$$
Polyether or polyester; Diisocyanate
$$[-O-R-O-\overset{\displaystyle O}{\overset{\|}{C}}-NH-R'-NH-\overset{\displaystyle O}{\overset{\|}{C}}]_n$$

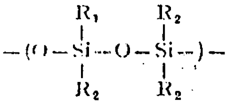
If the functionality of the hydroxyl or isocyanate (e.g. triisocyanate or trihydric alcohol) component is increased to 3 or more, branched or cross-linked polymers are formed. The properties of the reaction products can be controlled by the number of reactive groups in the hydroxy and isocyanate compounds and their molecular structure. They can be varied over a wide range of spectrum and be tailored to meet diverse requirements centring around rigidity and flexibility, toughness and hardness, chemical resistance, and abrasion resistance.

The main applications of polyurethanes in leather making are as urethane patent lacquers and impregnants. The principal purpose of leather impregnation with polyurethane, like other impregnants, is to upgrade various portions of low quality hide[92]. The use of polyurethanes for upgrading leather by impregnation was proposed in a US patent specification[93]. In this process, a prepolymer is made by reacting a diol with twice as many moles of a diisocyanate. This is then further reacted with a deficit of a diol or polyol (castor oil), so that the result is an isocyanate-terminated prepolymer. During the reaction, non-reactive solvents, such as cellulose acetate, toluene, butyl acetate, etc., are added to thin down the reaction mass. This prepolymer solution is applied by means of a curtain coater. The most important solvent-based urethane impregnants were described by Neher *et al.*[94,95] and Lowell *et al.*[96]. Grief[83], Dolnick[84] and Bosedon[97] discussed the solvent impregnation of leathers using polyurethanes. The advantages and disadvantages of polyurethanes and polyacrylic impregnant systems from the theoretical and practical viewpoints were compared by Donath[88]. Acrylic polymers are aqueous based as compared to polyurethane, which are solvent based. As compared to the weak bondage of acrylics to the leather by van der Waals forces, urethane prepolymers polymerize further to form a chemical bondage within the leather through the reactive isocyanate groups. Levy[98] also reported that the prepolymer reacts with the moisture in the atmosphere and the leather to form an extended polymer within the leather. The current uses of polyurethane impregnation and patent leather finishes, and the methods of using different types of urethanes, such as two-package curing materials, fast drying moisture-cure systems, and linear polymers have been discussed by Donath[99] in detail. The application of polyurethanes in leather processing has been recently reviewed by Speicher[67], Ossoff[68] and Kedlaya *et al.*[69]. In the past few years, substantial improvements have been made in practical application methods, especially as tanneries gained proficiency in the use of solvent system treatments. In the solvent based urethane impregnations, the type of leather tannage, fat liquor, etc., must be taken into account in preparing the above solution. The evaporation rates of solvents and the quantity of resin solids to be deposited must be linked with the past history of the hides and skins. Properly impregnated leather will not become progressively firm upon aging or develop a tendency to crack, but will remain flexible. A vast improvement in break, scuff and abrasion resistance and appearance will be obtained. The water vapour permeability is not affected, but remains in the same range as before. However, excessive laydown worsens the break, causing the leather to be coarser. The applications of polyurethanes as leather finishing agents are discussed under the head 'Finishing Agents'.

Silicones

The similarities existing between the silicon and carbon atoms have prompted rather widespread substitution of silicon for carbon, both in monomeric and polymeric compositions. Although carbon and silicon are similar in bonding geometry[37] and the usual SP^3 bonding characteristics[14-24], the differences in size, electronegativity and the availability of third orbitals in silicon provide organosilicones with rather unique characteristics.

These characteristics, as related to polymer compositions, provide some advantages to the polymer scientist in designing high performance coatings. Organosilicon compounds may be regarded as substitution products of silicon tetrachloride and they are called silanes by analogy with methane[43]. Chlorosilanes hydrolyse readily, giving products which in turn may split off water to yield compounds containing the siloxane link (Si-O-Si). The most commonly used polymers of this type are represented as:



$$-\left(O-\underset{R_2}{\overset{R_1}{Si}}-O-\underset{R_2}{\overset{R_2}{Si}}-\right)-$$

$R_1=H-;\ R_2=CH_3-$

$R_1=R_2=CH_3-$

$R_1=CH_3-;\ R_2=C_6H_5-$

$R_1=R_2=C_6H_5$

A large number of compounds with widely varying molecular weights can thus be produced with the lower silicones being referred to as silicone oils and the high molecular weight polymers called 'silicone greases' or 'rubbers'. Some of the advantages of silicone polymers consisting of stable siloxane repeating units are: greater heat stability, enhanced water resistance, antifoaming characteristics, excellent gloss retention, low thermal coefficient of expansion, excellent dielectric properties and greater adhesion to polar surfaces. It is thus not surprising that silicone polymers find wide application in leather industry.

In the leather industry, the use of silicones as water repellents has attracted considerable attention. Presently, there are several commercial products available for the treatment of leather. There are two main methods used for applying silicones to leather, viz. the solvent system and the aqueous system. In the solvent system, the leather is treated just prior to the end of the processing cycle. In the aqueous system, the silicone material is applied during the fatliquor operation. Both the systems impart water resistance to the leather, but for the successful use of either method, it is essential that the substrate be properly prepared. Depending upon the leather processing, the type of hide or skin used, and the degree of water resistance desired, the formulation can be adjusted for solids content to obtain the optimum treatment. Recently, Brown[69] discussed exhaustively the various recent methods of application of silicone resins in combination with glutaraldehyde. Various advantages of the silicone treated leathers over the conventional leathers were also discussed. Other applications of silicones in sole leather, mechanical leather, garment leather and other leathers were also described. Pastuska[100] discussed the improvement in the water proofing property of leather by silicones in combination with formaldehyde. Heit[101] produced side leather by using an aldehyde-silicone combination fatliquor on chrome tanned sides. The silicone gave good resistance to water penetration, the degree of resistance depending on the type of leather treated. A post-treatment with the conventional silicone solvent system imparted a high measure of water resistance. Physical characteristics, such as appearance, colour and shape retention, were better on the leathers treated in the above way. Serviceability was also improved, as measured by resistance to deterioration from artificial perspiration.

The efficiency of water repellent agents, such as silicones was found to be markedly improved by retannage of chrome leather with glutaraldehyde[102,103]. Neher *et al.*[104] studied the water resistance of leather treated with alkenyl succinic acid in combination with commercial silicone water proofing agents. Generally, the silicones used for water repellent treatment of leather contain a silicone resin or a silicone fluid[105]. Other types of organosilicon compounds have also been used in leather industry to impart water repellency. Chelates[106] obtained by the treatment of β-diketones or β-ketoesters with reactive zirconium compounds when applied to leather surface imparted them satisfactory water repellency. Water-soluble organosilicon-chromium Werner coordination compounds[107] have also been used for waterproofing leather. Poly-mono-camphyl siloxane and polymonocyclohexyl siloxanes[108], when dissolved in organic solvents and applied to leather, impart water repellency to it. The elasticity of leather is increased when organosilicon compounds like tetraethoxysilane or phenyltricresoxysilane[109] are incorporated in cellulose based lacquers in coating leather. Maminov and Voronkov[110] and Maminov[111] investigated the suitability of several organosilicon compounds for water proofing leather. These compounds not only impart good water resistance, but also increase the hygienic properties of the treated leathers.

A very soft and highly water-shedding leather results when acetone dehydrated pelt or chrome tanned leather is impregnated with silicones[112]. The softness and the satisfactory impregnation are both due to the thorough subdivision of the fibre, i.e. exposure of fibrillary surfaces. The use of silicones for waterproofing of leathers of different types was also discussed by Glozic *et al.*[113] and Morgan[114]. The use of solvent silicones provided a reliable method of obtaining a substantial improvement in the water repellency of chrome tanned side and upper leathers. Although silicones will give excellent results for waterproofing of leather, from many investigations, it appears that the effectiveness of a silicone treatment slowly decreases during service and this is probably due to gradual migration of the agent to the surfaces of the leather where it is rubbed off easily. However, wear trials indicate that this migration is not spontaneous, but is caused by polishing and wetting of the uppers during wear. If the silicone is chemically bonded to the leather fibres, this migration would not, of course, take place. This bonding can be brought about in many ways, such as incorporation of certain organometallic compounds in the silicone solution, or a diisocyanate, etc. Since silicones are expensive, the broad aim of future work must clearly be towards the development of treatments that are both cheap and effective.

Polysulphides

The polysulphide liquid polymers were developed in 1943. One of the earliest ideas was to investigate the use of these polymers for improving the properties of leather goods. Soon it was found possible to fill the voids in leather and convert the liquid polymer to the rubbery state in place. Various studies[115-119] were carried out on the application of this combination of leather and synthetic rubber for the improvement of water, oil and abrasion resistance of leather. The main repeating segment in the polysulphide polymer is the formal disulphide unit produced by the interaction of *bis*-2-chloroethylformal and sodium disulphide. However, 2% trifunctional reagent in the form of trichloropropane is added in the original reaction to develop crosslinks or branch chains along the sides of the main chain. Basic polysulphide liquid polymer structure may be represented as follows:

$$\mathrm{HS{-}(C{-}C{-}O{-}C{-}O{-}C{-}C{-}S{-}S){-}C{-}C{-}O{-}C{-}O{-}C{-}C{-}SH}$$

The chemistry[25-27,44] of the conversion reaction centres around the reactivity of the thiol (–SH) terminals and the thiol side chain groups. Leather hydraulic packings and oil seals impreganted with these polymers have performed satisfactorily in many industrial and automotive applications by combining the properties inherent in both leather and rubbers. Impregnation is accomplished by converting the liquid polymer to a rubber within the pores of leather and the solvent resistant elastomer is mechanically locked in place.

Application of Dibasic Acids

A waterproofing agent developed by Briggs[120] has the special feature of bonding firmly and permanently to chrome, the common leather tanning agent. The basis of the new development is to make leather waterproof by latching organic acids with chains of between 19 and 36 carbon atoms to the leather during the tanning process. The chains are flexible chromium complexes of high molecular weight.

Polyamides

Loose-grained upper leather can be improved not only through the incorporation of products already in common use in leather industry, but also with polyamides and polymers produced *in situ* by some sort of interfacial polycondensation[121]. Grain looseness of upper leather can be equally stopped by the use of aqueous solutions of epichlorohydrin-blocked cationic precondensates of modified polyamides. In all these cases, well known techniques of surface impregnation can be applied. The main advantage of interfacial polycondensation (IFB) processes is in fact that they do their job not with preformed polymers but with monomeric compounds with less material and to some extent the depth of penetration into the leather can be better controlled. The mechanism of this grain strengthening action is analogous to interfacial polycondensation performed on wool, known as the Wurlan process[119].

Polymers as Leather Finishing Agents

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. 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 emphasize 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, used in the present-day leather industry may be broadly classified as follows: (1) Protein and natural finishes; (2) Latex finishes; (3) Lacquers and lacquer emulsions; (4) Polyester and polyamide resin finishes; (5) Fluorocarbon finishes; and (6) Other miscellaneous finishing agents.

Protein and Natural Finishes

Among the natural high polymeric materials widely used for finishing leathers are casein, shellac, waxes, egg and blood albumin, water-soluble gums, glue and gelatin.

Casein — Casein, a natural polymer[122] made of amino acids, is a product obtained from milk by suitable precipitation, washing, drying, etc. Casein is generally used in admixture with other substances, rarely by itself, because it alone does not possess all the properties necessary for giving the final characteristics and appearance to leather. The leathers are sprayed on the top with a casein formaldehyde mixture, which is supposed to give a hard surface, protecting the finish from abrasion and also making it, to some extent, fast to wet rubbing. Casein forms a hard, horny insoluble substance by reacting with formaldehyde. The reaction of formaldehyde which controls the fixation of protein finishes is dependent on the temperature and concentration of formaldehyde. The effect of this reaction on the type of leather substrate and pigment and of the formulation of the finish has been assessed[123]. Casein pigment finishes may be used as base coats under pigment finishes or as printing colours over lacquer base coats to get unusual effects. Casein finishes withstand high temperature under friction glazing and in plating and produce a very smooth handle. The disadvantages of using casein in leather finishing are its affinity to water and low contribution to flexural endurance of the leather. The surface of the leather may become too brittle by excess spraying of casein. Other applications of casein in leather industry are for clarifying vegetable tanning solutions, as an ingredient of the paste for pasting leather as a filler for loose portions of leather, etc. With the development of synthetic high polymers, the application of protein finishes in the leather field has been offset to a great extent. However, attempts have been made in recent years to graft casein[124-129], gelatin[130-138] (and also Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., unpublished results) and other inedible proteins[139] with vinyl acrylic polymers and these products have been tried as binders and leather dressing materials. It was claimed that the film performance of these modified proteins is better and they are also more economical compared to nitrocellulose lacquers for finishing leather.

Shellac — Shellac[140,141] is another important finishing binder for leather. Though it finds considerable use along with other auxiliaries in leather finishing, its use as an independent material is limited due to its hard nature. At present, its application is limited to glaze finishes as an ingredient of protein finishes. It has been reported recently that the shellac can be made to graft copolymerize with vinyl monomers[142-145] to produce copolymers with improved film properties. The resulting products showed improved properties of film formation, such as hardness, flexibility and resistance to water and other solvents. The colour is the main limiting factor in the application of shellac resin as a binder for white leathers. The improved film properties of grafted products may find better applications for them in leather finishing.

Gelatine and glue — Gelatine and glue are degraded products of collagen, the latter being a more crude form. Gelatine or glue is added as an ingredient in certain pigment finish formulations that are intended to be harder in nature and capable of being friction glazed. They have very good adhesion power and dispersion capacity. Sufficiently plasticized, they can be used in glazed uppers and linings in limited quantities. Gelatine or glue is used in considerable quantities for leather finishing, as an emulsifying agent for fat liquors and for resurfacing buffing wheels with emery.

Egg/blood albumin — Albumins are hard and brittle drying protein binders which give high gloss on being friction glazed. They are very popular for the finishing of glazed upper leathers.

Gums, waxes and greases — Linseed mucilage is a popular bottom coat in the finishing of highly absorbent vegetable tanned leathers. It gives a very soft film on leather and prevents excessive absorption of the resin. Other gums like gum tragacanth, carboxymethyl cellulose, etc., also find limited applications in leather finishing. The wax from lotus leaves has been recently claimed[146] to impart water resistance to leather. The use of sugarcane wax for shoe polishes has also been reported[147,148].

Wax emulsions are important in leather finishing, as they impart to leather a smooth and waxy feel. In friction glazing, they help to produce good gloss and reduce the friction in between gloss and leathers. They act as releasing agents in hot plating of leather, when used in resin formulations. Carnauba wax is the widely used wax for this purpose.

Greases, alone and in combination with oils and waxes, have long been applied to leather to protect the fibres against damage by water and to improve water repellency. However, for effective waterproofing, large amounts of grease are required, which may fill the pores of the leather, so that the permeability to water vapour is extremely small and the leather is uncomfortable to wear.

Rubber latex and chlorinated rubber — Rubber latex is a natural emulsion of rubber in a slightly alkaline or aqueous medium. It has sometimes been used for finishing heavily buffed low grade leathers and splits. The main disadvantage of this material is its stickiness and relative instability. However, modified rubber latexes may be used for finishing upper leathers, overcoming the above disadvantages. Chlorinated rubber, when applied to leathers, forms films which are resistant to alkali and acid, and hence it may find an application in making speciality leather for extremely corrosive conditions.

Although there are many disadvantages of using these natural polymeric materials, they still find application for producing best leathers which maintain their natural character.

Latex Finishes

The latex systems and dispersions of resins in an emulsion form are, by far, the largest and most widely used means of preparing leather finishes today. The versatility, low cost and ease of application of these systems have led to their widespread use in the leather industry. The flammability and toxicity of organic solvents are largely avoidable; the film can be diluted with water, enabling thin films to be applied. In addition, the molecular weight of a polymer produced in the emulsion process is much higher than that of the polymer produced in the solvent process. The higher molecular weight in turn results in a better tensile strength and break modulus, better solvent resistance and high melting point, which gives a better ironing resistance to the film applied on leather.

Acrylic polymers — Among the latex polymers, the acrylics have unique advantages[149]. The flexibility, exceptional light fastness, absence of discoloration on ageing or exposure, toughness, pigment binding capacity, moulding ability, water resistance and compatibility with other synthetic resins are some of the striking properties of acrylic emulsions, which are highly desirable for use in leather finishing. The polymer chemist can select a great number of acrylic monomers for use in preparing the polymers, so that he can tailor-make the latex for each special end use. The formulation flexibility of acrylic polymers is unmatched among polymeric materials used in leather finishing. It is thus easy to understand why acrylic latex polymers gained their dominant role in upgrading and finishing leather.

The acrylic ester resins are copolymers of acrylic and methacrylic acids, and range in physical properties from soft elastomers having very high elongation to hard plastics. The harder resins find very good use in top coat formulations. The elastic acrylic polymers are applied as base coats for subsequent coats of lacquer finishes. In coating or finishing applications in which acrylic ester polymer emulsions are employed, an important factor is the "minimum film forming temperature" (MFT), the minimum temperature at which the polymer emulsion can deposit a continuous film[150,151]. The pigment binding capacity of the acrylic dispersions is employed with good effect in the highly pigmented systems employed for filling and covering, especially on leathers finished in pastel shades. Acrylic dispersion finishing systems find their main use in shoe uppers, leather goods and gloving leathers as a base coat. The acrylic resins used for these leathers show excellent adhesion and also have very good flexibility. Another application of polymer dispersions of the acrylic ester type is in shoe dressings to produce scuff-resistant leather. The use of resin finish systems based on emulsions and pigments has increased with the increased mechanization of the leather industry and with increasing advances made in polymer chemistry for forming copolymers to give different lattices which have a broad spectrum of properties. A wide variety of polymer emulsions has been used or proposed for leather finishing[152-154] The basic textbook of Mudd[155] has been supplemented by a series of papers on resin emulsions. Naidus *et al.*[156] have classified the monomers according to the hardness of the polymers produced, while Handscomb[157] has investigated some of these chemical types in finishes. Nutt[158,159] dealt with the compositions of films used in finishing a wide variety of leathers. He also investigated[160] resin finishes modified by the addition of casein and wax and the influence of charge on the physical properties of the applied finish. Spiers and Burnett[161] investigated the wet rubfastness of resin protein finishes. Landmann[162,163] has shown that the nature of the fat liquor has a considerable effect on some of the characteristics of a predominantly resin leather finish. He also studied[164] how the variations in tannage have been held responsible for large variations in the application and ultimate appearance of finished leather. Sharphouse and Jalaluddin[165] investigated the part played by the leather surface in leather finishing by acrylic polymer dispersions. Landmann and Sofia[166] recently studied the effect of retannage and the nature of finish on water vapour permeability and other characteristics of the finished leather. Resin finish systems based on emulsions and pigments were useful in imparting different types of colours to leather and in giving leathers of uniform quality at low cost. With the aid of acrylic finishing and impregnating materials, it is possible to exploit fully the inherent natural advantages of leather and to upgrade leather to an extent that was not deemed to be possible a decade ago.

Lacquers and Lacquer Emulsions

Lacquers are generally defined as coating systems which produce films by solvent evaporation. Basically, three main types of lacquers are used in leather finishing, classified[54,55,167-169] by the nature of the film-forming material they contian. They are: (1) nitrocellulose, (2) polyurethane, and (3) vinyl lacquers.

Nitrocellulose Lacquers

Cellulosic polymers[1,170,171] such as nitrocellulose and other esters of cellulose have been used for a long time as coating materials for leather. Cellulose, the raw material from which the cellulosic polymers are made, is the chief constituent of living plants and is a natural high polymeric material formed by the condensation of glucose molecules. These polymers are very good film-forming materials because of their inherent qualities of fast air drying and film strength. These properties are derived from their high molecular weight and their relatively high softening point. Lacquers are made from cellulose esters by evaporation of solvent, leaving behind a hard tough film on the surface. The speed of drying depends mainly on the type of solvent used. The cellulosic polymers are tough, horny solids and are available in a wide range of molecular weights. Among the cellulosic polymers, cellulose nitrate, cellulose acetate, and cellulose acetate-butyrate find wide applications in the leather industry.

Cellulose nitrate (nitrocellulose) — The most commonly used lacquer based on cellulosic polymers used in leather finishing is nitrocellulose[172-174]. Nitrocellulose lacquers are available in different forms: (i) straight lacquers with no water content, (ii) solvent emulsion with a small amount of water and emulsifying agent, and (iii) water emulsion, which gives a very continuous film of lower application cost. Nitrocellulose lacquers of types (ii) and (iii) are widely used in the leather industry. Plasticizers are essential ingredients in the lacquer formulations, as nitrocellulose by itself has inferior film properties. Some of the advantages of nitrocellulose lacquers are ease of application, quick drying, non-tacky and glossy surface, fastness to dry and wet rubbing, water resistance, and better flexibility of the film. Nitrocellulose lacquers have a very good compatibility with the acrylic base coats. The main drawback limiting their universal application to leather is their poor light fastness. The use of nitrocellulose lacquers in leather finishing is increasing nowadays.

Cellulose acetate — The viscosity properties of these polymers are more or less same as those of nitrocellulose, but they are more heat resistant and transmit ultraviolet light freely. Their disadvantages are poor compatibility with plasticizers and other film-forming materials, sensitivity to absorption of moisture and lack of solubility in many organic solvents.

Cellulose acetate-butyrates — Cellulose acetate-butyrates (CAB) are mixed esters of cellulose, they have somewhat better solubility and compatibility than cellulose acetate, but are not as good as the nitrocellulose. The properties of the lacquer-type cellulose acetate-butyrates have been discussed in detail by Malm and Smith[175]. These polymers are used for leather, particularly non-yellowing lacquers for white and pastel shade leathers. The increase in the butyryl content increases solubility, tolerance for diluents, compatibility for plasticizers, flexibility and moisture resistance, but melting point, tensile strength and hardness decrease with increase in butyryl content. Non-yellowing water white lacquers with very desirable properties can be prepared with modification by acrylic resins and urea-formaldehyde resins.

Polyurethane Lacquers

The chemical industry is constantly developing new polymers for surface coating applications and the development of polyurethanes, for example, has made available a wide range of lacquers. Patent leather provides the largest field of application of polyurethanes for leather nowadays. Polyurethane finishing became possible in 1954 and since 1958, it has been in practical use to an increasing extent. Patent leather today can be produced in any leather factory, using leather from normal production and without expensive and cumbersome solvent degreasing units. This is no longer the mysterious yet highly profitable domain of a few specialized tanners nor does it depend on special experience. In the patent leather field, the high build of urethane coatings, giving the desired high gloss, is the important property. Drying is based partially on the evaporation of solvents and more importantly on curing, which in effect is the reaction between the —NCO— group and the free hydroxyl groups. The advantages of the system, in addition to the obvious high gloss and the quality of the patent look are outstanding flexibility, solvent and water resistance as well as low temperature flexibility. The chemistry of formulation and application of polyurethane lacquers on leathers was the subject of many investigations[12,54-58,176-181]. Huang[62] recently discussed the general urethane chemistry, type of coatings suitable for leather application, formulation variables, and practical problems associated in the application of these coatings. Donath[99] also discussed the general properties, usefulness and history of urethane polymers. The basic chemistry involved in their formulation, properties of particular usefulness in the leather finishing are considered, with special reference to scuff resistance, toughness of films formed, flexibility at all temperatures and gloss. Current uses in impregnation and patent leather finishes are dealt with in detail and additional fields where properties of these polymers can be put to most advantageous use have also been examined. Methods of using the different types of urethanes, such as two-package curing materials, fast drying moisture-cure systems and linear polymers have been described. Arbaud[182,183] recently reported a new type of polyurethane elastomers prepared by the reaction of polyisocyanate with amines, which have useful properties of drying, adhesion and firmness. The new application avoids harmful solvents, diluents, catalysts and binders. Pulles[184], Speicher[57] and Ossoff[68] recently reviewed the various developments in polyurethanes and their wide applications in finishing and impregnation of leather. Some of the latest developments in polyurethane applications in leather are briefly discussed below.

Reactive polyurethane coating — This process[57] constitutes a very hopeful prospect for the future, since it permits the use of splits and less costly leathers to produce, for instance, kid imitations of perfectly natural appearance and with excellent wearing qualities.

Fully reacted urethane polymer — Fully reacted urethane polymers found their applications[184] not only on full grain leathers but also on corrected grain leathers where high requirements of physical resistance are needed. The fact that these products may be applied to leather as well as to synthetics, throws open an entirely new field of application, viz. that of shoe dressings.

Easy care finishes — Recently, the field of easy care finishing[185-187] has attracted the attention of leather chemists through the development of aqueous dispersions of weakly reactive polyurethanes. An important advantage of "wet look" leathers[188], in addition to high gloss, is that they are truly clean. They are dirt resistant and are truly wipe and wear. The new type of polyurethane dispersion has also been successfully used in regular finishing to improve crack fastness and scuff resistance, and also as an adhesion-improving agent. The easy care process is well established for top quality nappa and in particular for upholstery and clothing leathers. Two component lacquers give coatings which withstand even extreme stress, with films that are not softened or damaged by the generally used solvents or concentrated alcohol, and yet retain the aniline character of full grain leather.

Microporous polyurethane foils — Leather coated with microporous polyurethane foil has been recently introduced[189] in the market. A suitable adhesive is applied to splits, buffed or skivered grain leathers in such a way that permeability is preserved. Then the foil is applied and printed or plated immediately. This is followed by finishing on normal automatic spraying equipment. Leathers coated with microporous polyurethane foil are considerably superior to any leather substitute or the so-called man-made leathers.

Vinyl Lacquers

Vinyl lacquers consist of solutions of vinyl polymers and copolymers in suitable solvents[1,6-9]. These vinyl lacquers are mostly used in finishing upholstery leather[190] for producing films with superior abrasion resistance. Although vinyl finishes are an improvement over the conventional finishes, their properties are certainly next best to the urethane finishing as far as scuff and abrasion resistance are concerned. The leathers finished with vinyl lacquers are more resistant to snow and water. One other advantage of vinyl finishing is its low cost compared to urethane finishing.

Polyester and Polyamide Resins

Polyester resins are made from polybasic acids and polyhydric alcohols[36-40], one of which contains C=C unsaturation. This permits crosslinking with unsaturated materials to form a partially thermosetting product. Alkyd resins[1,3,35,191] are essentially polyesters which are modified with drying or non-drying oils as well as natural and synthetic resins. Alkyd resins are extensively used in paint and printing ink industry but they find limited use in leather industry due to the poor flexibility of their film and comparatively longer time for drying. The leathers finished with alkyd resins have exceptional surface properties, such as fastness to dry and wet rubbing, good and uniform gloss with a very smooth finished surface. Recently, attempts were made[3] to copolymerize alkyd resins (oil modified) with acrylic monomers in order to impart more flexibility and adhesion of the film to the leather.

Polyamides are condensation products of diamines and dicarboxylic acids[34]. They have good abrasion resistance, perspiration resistance and toughness. They are extensively used for finishing upholstery leathers, such as horse saddles, etc. Due to their limited solubility in organic solvents, low flexibility and high cost, they are not very popular in the leather finishing industry. Advances in leather finishes based on alkyd resins have been reviewed recently by Vedarajan *et al.*[53].

Fluorocarbon Finishes

A very interesting field of polymers and relatively new branch of finishing agents for leather are the fluoro chemicals[192]. Substitution of the fluorine atom for hydrogen in certain organic compounds imparts to them a property of intense surface repellency both against water and oil. 'Scotch gard', 'Zepel' and 'Pentel' are some of the popular brand names of these compounds. Although the active content of these compounds is not well known, they are considered to be polymers of fluorinated acrylic and vinyl compounds. These polymerized polyfluoryl acrylic or vinyl polymers could either be aqueous or solvent based. They can be applied to leather like the acrylic polymers. The use of fluorocarbon finishes in leather has been claimed to impart resistance to acids and alkalis, repellency to water and oil and perspiration resistance, apart from the lubricating effect. Other advantages include good handle, fine break, greater porosity, more comfort, lighter weight and greater flexibility endurance at extreme temperatures. Chrome, zirconium and alum tanned leathers may give better results with these compounds as compared to straight vegetable tanned leathers, which are likely to react with the fluorochemicals. These finishes are expensive, but ways have been found to use them in conjugation with cheaper water repellents to lower their overall cost. In two recent brief reviews[193,194], the properties of fluorochemically treated leathers and the benefits of such treatments have been discussed.

Other Miscellaneous Finishing Agents

Water-soluble polymers, such as cellulose ethers, pectins and alginates are often used for different finishing applications in leather. In a recent brief review[195], various applications of alginates in leather processing have been discussed. The colloidal properties of water-soluble alginates make them useful in various leather finishing processes. Alginate treatment prior to dyeing increases the penetration of the dyestuff, offers level dyeing, and improves the feel and handle of the leather. Triethanolamine alginate, when used as a grain filler, prevents the migration of the plasticizer from the finish into the leather. Sodium or ammonium alginate when added to finishes containing emulsified oils and/or pigments improves emulsion stability and the finish. Propylene glycol alginate is excellent as a protective colloid in cationic fat liquor emulsions. Calcium alginate in conjugation with starch or casein serves as a good paste drying material. Sodium alginate is best suited for sole leather when used alone or along with epsom salt, as it prevents the migration of tannin to the surface during drying. A wide range of alginates for industrial use are commercially available now.

Future developments in the theory and practice of polymer chemistry will have considerable impact on the leather finishing industry. New copolymers of the random, block or graft type will bring to the finishing and coating fields entirely new sets of properties. The interaction of the chemistry of thermoplastic systems with that of thermosetting systems results in an entirely new group of attainable properties as well as processes. The tailor-making of polymer structures to incorporate specific properties will lead to the utilization of numerous finishing materials with different properties for a particular end use. Not only new synthetic polymeric materials but also new materials based upon suitable chemical modifications of naturally occurring resins will be brought in future in the coating/finishing field.

Polymers as Tanning Agents

Synthetic, as well as natural polymeric materials, have been used[196] in leather processing and tanning for a long time to obtain special effects.

Polyaldehydes and Aldehyde Resins

Formaldehyde resins — It has been known for a long time that formaldehyde and certain other aldehydes are active tanning agents[197]. The condensation products of polyhydric phenol, such as resorcinol with formaldehyde were found to be effective tanning agents by polymerizing them *in situ* in hides and skins[198,199]. This procedure was later extended[200-205] to include tetrakis (hydroxy methyl) phosphonium chloride and tris(hydroxy methyl)nitromethane with resorcinol. These tannages produced leather of saleable quality that had a high hydrothermal stability. The commercial availability[206] of an acroleinformaldehyde polymer led to an investigation of its reaction with resorcinol, using the same procedure. Good quality sheep skin lining and work-glove leather were produced using the above resin[207,208].

The amino resins[30,106], such as urea and melamine resins, are the most prominent members which find important applications in leather industry. These are the condensation products of formaldehyde. Leathers tanned with urea resins are pure white, perfectly light fast, resistant to the actions of acids and alkalies, and can be dyed with most of the acid or direct dyes. The main disadvantage in the use of urea resins is of high and rapid water absorption. Melamine resins are used to impart desirable characteristics to white and coloured leathers. Improvements in break, grain thickness and strength, as well as development of fulness of flanks and bellies without increased amounts of tanning extracts are made possible by the use of small amounts of melamine resin. The condensation products of dicyandiamide and formaldehyde are also used as tanning agents[209] in leather industry.

Polyaldehydes — The commercial availability of certain polyfunctional aldehydes in recent years has created considerable interest regarding their use as tanning agents. The dialdehyde-resin tannage was first developed by Winhein and Doherty[210]. Seligsberger and Sadlier[211] and Fein and Filachione[212] studied the tanning action of straight-chain aliphatic dialdehydes. The tanning properties of glutaraldehyde[213], dialdehyde starch[214-218], dialdehyde alginic acid[219] and dialdehyde cellulose have been investigated by different workers. These compounds have been recommended as pretanning agents for sole leather and also for the manufacture of garment leather. Some of these compounds are, however, only of theoretical interest, while some may well have a commercial future, depending mainly on the cost of the raw materials.

Vinyl and Acrylic Polymers

Acrylic syntans — Acrylic syntans have great versatility and can be used in almost all such uses where a plump durable leather is required. The advantages of using acrylic syntans for tanning in combination with other tanning materials have been discussed in detail by Porter and Davis[220]. The optimum conditions for obtaining the most favourable results in the retanning of chrome leather are discussed. For best results, the sequential use of syntan, acrylic resin followed by vegetable tannins is recommended. Preformed polymers of acrylic acid and methacrylic acids have also been used for tanning hides and skins[221,222].

Styrene-maleic anhydride copolymers — Styrene-maleic anhydride copolymers have been in use in tanning hides and skins for a long time. Many commercial products based on these copolymers find wide applications in leather industry for tanning leathers. The sodium salt of the maleic copolymer is used in making white and coloured leather, including sheep skin and kid skin, grains and suedes, as well as side leather. The styrene-maleic anhydride copolymers may also be used as retanning agents. The sulphonated products of this copolymer are specially useful[223,224] in bleaching chrome tanned leather. Vinyl derivatives were introduced into the hide as emulsions and the absorbed monomers polymerized *in situ*[225]. An excellent rot proofing treatment of hides or leather has been developed by the *in situ* polymerization of acrylonitrile and acrylic acid[226,227]. Bandert *et al.*[228] have shown that the polymerization of vinyl monomers in the midst of hides and skins confers waterproof and rot proof qualities to leather. In most of these cases, it is rather apparent that the polymers are only physically deposited in the voids of leather.

Polyepoxy Resins

Polyepoxides, the condensation products of epichlorohydrin and bisphenol-A have also been used as tanning agents for the production of white leathers[220-232]. A wide range of similar leathers have been produced from materials, such as butadiene dioxide, acetyl ethylene oxide, etc., whose common feature is two active groups capable of reacting with collagen[28]. Tanning with epoxy resins resulted in lower stretch and greater stiffness in flexure than conventionally chrome and vegetable tanned leathers. The leather obtained by tanning with these resins showed a high reversible shrinkage (T_s, 85°C). But this type of tannage resulted in considerable loss of strength compared with chrome and vegetable tannage.

Diisocynates

Diisocynates as tanning material have been studied in Germany since 1937; however, only a limited number of them have found practical use. The diisocynates are formed by the reaction between a diamine and phosgene

$$H_2N-(CH_2)_2-NH_2+2COCl_2 \rightarrow$$
$$OCN-(CH_2)_n-NCO+4HCl$$

Diisocynates can be used for tanning in aqueous solution, because they have a stronger affinity for amino groups than for water. A method for tanning with isocynate compounds in non-aqueous solutions has been patented by Putnam[233]. Polymers obtained from monomers of the formula $CH_2=CH$-Ar-NCO react with the leather[234]. Reaction with isocyanates introduces into collagen new groups, which subsequently enter into the polymerization reaction[235]. Reactive polymers containing free isocyanate groups may form a covalent bond with the leather. High cost and very high toxicity are the two main disadvantages limiting the application of these compounds as tanning materials in the leather industry.

Acrylate-chrome Complexes

Recently, trinuclear aluminium and chromium-acrylate complexes were prepared and used[236-238] (also Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., unpublished work) for tanning hides and skins. Attempts were made to polymerize these acrylates subsequently taking advantage of the vinyl double bond using redox type initiation.

Miscellaneous Tannages

One of the oldest known tannage is the oil tannage, which utilizes semi-drying fish oils and is nowadays used mainly in the manufacture of chamois leather. During the second world war, a synthetic chamois tannage based on aliphatic sulphonyl chloride (Immergan) was developed in Germany. It yielded a white leather that dyes well and can be cleaned with solvents or by washing, making it suitable for gloving and other clothing leathers. Recently, a number of papers have appeared in this field, which have been reviewed by Olivannan and Nayudamma[239].

Although tanning with polymeric materials could not receive wide attention, the developments in the polymer science may give rise to newer and modified products, which may find various applications individually or in conjugation with other tanning materials in leather industry.

Grafting of Synthetic Polymers on Hides, Skins and Leathers

Graft copolymerization is a novel method[240], which has wide applications in synthesizing new forms of polymeric materials and also in modifying the properties of natural and synthetic polymers. A graft copolymer comprises a high molecular weight backbone to which a second polymer is attached at intervals along the chain. The backbone may be homopolymeric or copolymeric with pendent groups of either type. Graft copolymerization is different from random or block copolymerization in that it leaves the main polymeric substrate backbone essentially intact. A graft copolymer combines some of the characteristic properties of each polymer or possesses properties entirely different from those of either of the components. Hence, such products made up of selected polymer combination can have highly specific properties tailor-made for a particular end use. Exhaustive studies[241-250] have been carried out in our laboratory for the last few years on the modification of collagen, a heterogeneous natural polymer by graft copolymerization with vinyl monomers. Methods were developed for the first time in our laboratory for the grafting of different vinyl monomers on collagen, hides and skins, and leathers using ceric ion initiation technique. These methods were later extended successfully for grafting on hides, skins and leathers in the tannery on a larger scale using a number of hides and skins, and it has been found that the laboratory methods can be successfully extrapolated to the tannery scale. The results obtained in these studies show that grafting could be accomplished by combining the good qualities of both the synthetics and natural fibres without affecting the water vapour permeability of the leather. The grafted leathers were full and showed improved properties, such as decreased water absorption, increased resistance to acids and alkalies, resistance to rot and mildew, improved light fastness of the dyed leathers, improved gloss of the finished leathers without detracting from the favourable properties of leathers produced in the conventional way. The leathers grafted with polybutyl acrylate were found to be the best. The leather was very full and the elongation was increased twofold without a decrease in tensile strength. The properties of the grafted leathers were found to depend on such factors as the monomer used, the type of initiator, the distribution of vinyl polymer in the protein structure, and the molecular weight of the grafted polymer chains. It is possible to correctly choose a polymer type depending upon practical requirements. The monomers should be so selected that the polymer grafted could improve the wear of leather without detracting from the favourable properties of the natural leather. The choice of monomer(s) is particularly significant, since it has a major influence on many of the desirable properties of the grafted skin collagen and on the formulated leather properties. Since no single polymer grafted could give all the desirable properties, which may be enumerated, compromises must be made to obtain the most desirable properties of the grafted polymer branch chains. These compromises were best achieved by polymerizing monomeric mixtures to form grafted side chains on the collagen backbone.

Impregnation or coating of leather with various preformed polymers to overcome some of the deficiencies of leather is a common practice, which was discussed in the earlier sections. Unfortunately, these treatments result in uneven deposition of the polymer, mainly on the surfaces of the substrate which are washed away during use, because they are only deposited in or on the leather and are not covalently attached. In some cases, some of the more desirable properties of the leather suffer as a result of these treatments. Grafting hides, skins and leathers with polymers, on the other hand, resulted in more even distribution of polymer throughout the substrate by covalent bonding, which cannot be removed by any physical means. Chemical and physical characterization of the collagen-graft copolymers revealed that only a small number of initiation and grafting sites are present in collagen. The smaller involvement of the fibre molecules in the grafting reaction means that substantial percentage of grafted material can be added without sacrificing the well-known hygienic properties of leather. Nevertheless, the properties of grafted chains can be added to the leather. Thus, the grafting will be advantageous in imparting certain desirable properties to leather without causing major changes to the fibre itself.

Grafting of methyl methacrylate and other monomers on to collagen was reported by Studniarski and Hankiewcz[251] and also by Russian workers[252-257], but the reports are lacking in detail. The method of graft copolymerization for modifying hides and skins and producing functionally modified leathers[258] has now received much attention. Further extensive studies are, however, needed to determine the kind and extent of grafting required to obtain leathers with significant commercial potential. Studies are also needed to develop methods using cheap initiators, so that this process can be commercially exploited. Such studies are in progress at present in our laboratory. The graft compolymerization of vinyl monomers on to proteins in general has recently been reviewed by Panduranga Rao *et al.*[259] and Panduranga Rao[260]. Liquid polysulphides, which have been employed for a number of years as impregnants for leather, have been successfully grafted to certain types of leathers[261]. The reactive thio terminals of the polysulphides were coupled with different aldehyde tanned leathers. Polysulphide grafted leathers showed promising results compared to controls.

Synthetics in Footwear Industry

Substitute materials from the plastic and synthetic polymer industry have made deep inroads into the footwear field in recent years. The loss of markets for shoe sole leather is now well known and this is probably irrevocable. The poromeric materials which have substituted leather in the footwear industry were recently reviewed by Payne[262] and others[263-265]. The application of various synthetic polymers in the footwear industry have been reviewed recently by Moore[263] and Turner[267].

Future Trends

The survival of leather in competition with synthetics lies in the retention of leather as a preferred material in the eyes of the consumer and hence it must be constantly developed and improved to retain that status. Though leather by itself has many desirable properties, there are also many inherent defects, such as the lack of uniformity in quality, weight, susceptibility to chemical attack, poor scuff resistance and high water absorption. If history is a guide, like rubber and textiles, leather will be gradually displaced by synthetic materials, which are amenable to rapid improvement and mass production. This trend will soon start, if not already started. Research is, therefore, directly needed to maintain the competitive position of leather and to find new outlets for animal hides and skins. The appendage of side chains to collagen fibres may result in the formation of composite macromolecule whose properties may differ from those of the original collagen. Graft copolymerization thus yields a new tool to be used in the task of controlling and modifying molecular structure. Even though the possibilities of creating new polymers are not exhausted, the investigations into methods for modifying the existing materials are of utmost importance. Since the preparation of a graft copolymer represents a method of tailor-making polymeric molecule in order to incorporate the desired characteristics, the interest in and the importance of graft copolymerization is bound to grow and develop into a major area of research in the leather and glue industries.

Summary

The impact of polymers on leather science and industry is discussed. The applications of polymers in leather manufacture are described, with particular reference to recent developments. The grafting technique using synthetic polymers in improving the properties of leather is also discussed. The possible future developments in polymer chemistry, in so far as they concern leather industry, are indicated.

References

1. Payne, H. F., *Organic coating technology*, Vols I & II (John Wiley & Sons Inc., New York), 1964.
2. Mayers, R. R. & Long, J. S., *Film-forming compositions*, Vol. I (Marcel Dekker Inc., New York), 1969.
3. Solomon, D. H., *The chemistry of film formers* (John Wiley & Sons Inc., New York), 1967.
4. Gaynes, N. I., *Formulation of organic coatings* (D. Van Nostrand Co. Inc., New York), 1967.
5. Martens, C. R., *Technology of paints, varnishes and lacquers* (Reinhold Book Co. Inc., New York), 1968.
6. Riddle, E. H., *Monomeric acrylic esters* (Reinhold Publishing Co. Inc., New York), 1954.
7. Schildknecht, C. E., *Vinyl and related polymers* (John Wiley & Sons Inc., New York), 1963.
8. Leonard, E. C., *Vinyl and diene monomers* (Interscience John Wiley & Sons Inc., New York), 1970.
9. Tsuruta, T. & O'Driscoll, K. F., *Structure and mechanism in vinyl polymerizations* (Marcel Dekker Inc., New York), 1969.
10. Saunders, J. H. & Frisch, K. C., *Polyurethanes: chemistry and technology*, Vol. I & II (Interscience Publishers Inc., New York), 1964.
11. Dombrow, B. A., *Polyurethanes* (Reinhold Publishing Co. Inc., New York), 1965.
12. Phillips, L. N. & Parker, D. B. V., *Polyurethanes* (Iliffe Books Ltd, London), 1964.
13. Bruins, P. F., *Polyurethane technology* (Interscience Publishers Inc., New York), 1969.
14. Fordhams, S., *Silicones* (George Newnes Ltd, London), 1960.
15. Bazant, V., Chvalovsky, V. & Rathousky, J., *Organosilicon compounds* (Academic Press Inc., New York), 1965.
16. Meals, R. N. & Lewis, F. M., *Silicones* (Reinhold Publishing Co. Inc., New York), 1959.
17. Rochow, E. G., *Chemistry of the silicones* (John Wiley & Sons Inc., New York), 1951.
18. McGregor, R. R., *Silicones and their uses* (McGraw-Hill Book Co. Inc., New York), 1954.
19. Eaborn, C., *Organosilicon compounds* (Academic Press Inc., New York), 1960.
20. Freeman, G. G., *Silicones, an introduction to their chemistry and applications* (Iliffe Books Ltd, London), 1962.
21. Petrov, A. D., Mironot, B. F., Ponomarenko & Chernyshev, E. A., *Synthesis of organosilicon monomers* (Consultants Bureau, New York), 1964.
22. Voorhoeve, R. J. H., *Organohalosilanes* (Elsevier Publishing Co., Amsterdam), 1967.
23. Andrianov, K. A., *Metalorganic polymers* (Interscience Publishers Inc., New York), 1965.
24. Barry, A. J. & Beck, H. N., cited in *Inorganic polymers*, edited by Stone and W. A. G. Graham (Academic Press Inc., New York), 1962, Chap. 5.
25. Berenbaum, M. B., cited in *Polysulfide polymers*: I Chemistry: Polyethers, Part 3, edited by N. G. Gaylord (Interscience Publishers Inc., New York), 1962, Chap. 13.
26. Panek, J. R., cited in *Polysulfide polymers, II, Applications*: Polyethers, Part 3, edited by N. G. Gaylord (Interscience Publishers Inc., New York), 1962, Chap. 14.
27. Tobolsky, A. V. & Macknight, W. J., *Polymeric sulphur and related polymers* (Interscience Publishers Inc., New York), 1965.
28. Lee, H. & Nexille, K., *Handbook of epoxy resins* (McGraw-Hill Book Co. Inc., New York), 1966.
29. Skeist, I., *Epoxy resins* (Reinhold Publishing Co. Inc., New York), 1958.
30. Blais, J. F., *Amino resins* (Reinhold Publishing Co. Inc., New York), 1959.
31. Martin, R. W., *The chemistry of phenolic resins* (John Wiley & Sons Inc., New York), 1956.
32. Robitschek, P. & Lewin, A., *Phenolic resins* (Iliffe & Sons Ltd, London), 1950.
33. Whitehouse, A. A. K., Pritchett, E. G. K. & Barnett, G., *Phenolic resins* (Iliffe Books Ltd, London), 1967.
34. Floyd, D. E., *Polyamide resins* (Reinhold Publishing Co. Inc., New York), 1966.
35. Patton, T. C., *Alkyd resin technology* (Interscience Publishers Inc., New York), 1962.
36. Lawrence, J. R., *Polyester resins* (Reinhold Publishing Co. Inc., New York), 1960.
37. Bjorksten, J., Tovey, H., Harker, B. & Henning, J., *Polyesters and their applications* (Reinhold Publishing Co., New York), 1956.
38. Boenig, H., *Unsaturated polyesters: Structure and properties* (Elsevier Publishing Co., Amsterdam), 1964.
39. Goodman, I. & Rhys, J. A., *Polyesters, Vol. I: Saturated polymers* (Iliffe Books Ltd, London), 1965.
40. Parkyn, B., Lamb, F. & Clifton, B. V., *Polyesters, Vol. II: Unsaturated polyesters and polyester plasticizers* (Iliffe Books Ltd, London), 1967.
41. Brusie, J. P., cited in *Encyclopedia of polymer science and technology*, Vol. I (Intersceicne Publishers Inc., New York), 1964, 246.
42. Pigott, K. A., cited in *Encyclopedia of polymer science and technology*, Vol. II (Interscience Publishers Inc., New York), 1969, 506.
43. Lichtenwalner, H. K. & Sprung, M. N., *Silicones* cited in *Encyclopedia of polymer science and technology*, Vol. 12 (Interscience Publishers Inc., New York), 1970, 464.
44. Berenbaum, M. B., cited in *Encyclopedia of polymer science and technology*, Vol. 11 (Interscience Publishers Inc., New York), 1969, 425.
45. Lee, H. & Neville, K., cited in *Encyclopedia of polymer science and technology*, Vol. 6 (Interscience Publishers Inc., New York), 1967, 209.
46. Sweeny, W. & Zimmerman, J., cited in *Encyclopedia of polymer science and technology*, Vol. 10 (Interscience Publishers Inc., New York), 1969, 483.
47. Keutgen, W. A., *Phenolic resins*, cited in *Encyclopedia of polymer science and technology*, Vol. 10 (Interscience Publishers Inc., New York), 1969, 1.
48. Boening, H. V., cited in *Encyclopedia of polymer science and technology*, Vol. 11 (Interscience Publishers Inc., New York), 1969, 129; 62.
49. *Organosilicon chemistry, Special lectures presented at the International Symposium on organosilicon chemistry (IUPAC), Prague, Czechoslovakia*, 6-9 September 1965 (Butterworths Publishers Ltd, London), 1966.
50. *Organosilicon chemistry—Lectures presented at the Second International Symposium on organosilicon chemistry (IUPAC), Bordeaux, France*, 9-12 July 1968 (Butterworths Publishers, London), 1969.
51. Bruins, P. F., *Silicone technology, applied polymer science Symposia*, No. 14 (Wiley-Interscience Inc., New York), 1970.
52. Saroja, S., Subramaniam, V. V. & Nayudamma, Y., *Leath. Sci.*, 16 (1969), 115.
53. Vedarajan, R., Subramaniam, V. V. & Nayudamma, Y., *Leath. Sci.*, 16 (1969), 93.
54. Nijkamp, G., *Leath. Sci.*, 16 (1969), 223.
55. Venkatachalam, P. S., Singh, J. & Krishnan, T. S., *Leath. Sci.*, 16 (1969), 122.
56. Kedlaya, K. J., Ramaswamy, D. & Nayudamma, Y., *Leath. Sci.*, 18 (1971), 155.
57. Speicher, W., *Leath. Mfr.*, 89 (1972), 19.
58. Ossoff, J. A., *Leath. Mfr.*, 89 (1972), 18.
59. Brown, M., *Leath. and Shoes*, 153 (1967), 1.
60. Kedlaya, K. J., Rajadurai, S. & Ramaswamy, D., *Leath. Sci.*, 18 (1971), 309.
61. Vedarajan, R., Subramaniam, V. V., Rajadurai, S. & Huang, D. K., *Proceedings of the sixth tanners get-together* (Central Leather Research Institute, Madras), 1971, 146.
62. Huang, D. K., *Proceedings of the sixth tanners get-together* (Central Leather Research Institute, Madras), 1971, 141.

63. Bauer, W., *US Pat.* 1,829,208 (to Rohm & Haas A.G.), 27 October 1931; *Chem. Abstr.*, **26** (1932), 735.
64. Reppe, W., *Ann.*, **582** (1953), 1.
65. Fisher, G. J., *US Pat.* 2,844,622 (to Celanese Corporation of America), 22 July 1958; *Chem. Abstr.*, **52** (1958), 19951.
66. Crawford, J. W. C., *US Pat.* 2,101,821, 7 December 1937 (to Imperial Chemical Industries Ltd); *Chem. Abstr.*, **32** (1938), 951.
67. Weizmann, C., *US Pat.* 2,525,249 (to Polymerizable Products Ltd), 10 October 1950; *Chem. Abstr.*, **45** (1951), 1621.
68. Salkind, M., Riddle, E. H. & Keller, R. W., *Ind. Engng Chem.*, **51** (1959), 1232, 1328.
69. Lawler, P. V., *US Pat.* 2,763,577, 18 September 1956; *Chem. Abstr.*, **51** (1957), 2347.
70. Buechler, P. R., *Leath. Mfr.*, 78 (1961), 19.
71. Buechler, P. R., *Leath. Mfr.*, 79 (1962), 25.
72. Lowell, J. A. & Buechler, P. R. *J. Am. Leath. Chem. Ass.* **60** (1965) 519.
73. Brown G. L. & Grief M., Wetting and penetration of leather, communications, *Ninth Congress of the International Union of Leather Chemists Societies, Lyon (Rhone). France*, 1965, 115.
74. Quinn, L., *Leath. Mfr.*, **83** (1966), 30.
75. Shaw, R., *Leath. Shoes*, **146** (1963), 31.
76. Merken, M. & Katz, G. J., *Leath. Shoes*, 146 (1963), 20.
77. Christensen, B. F., *Leath. Mfr*, **82** (1965), 74.
78. Brueter, W., *Aust. Leath. Footwear Rev.*, **61** (1965), 21.
79. Rieger, W., *Tanner*, **20** (1965), 83.
80. Lowell, J. A., Hatton, H. L., Glavis, F. J. & Buechler, P. R., *US Pat.* 3,103,447, 10 September, 1963.
81. Mattei, I. V., *US Pat.* 3,269,858 (to Rohm & Haas Co.), 30 August 1966; *Belg. Pat.* 637,052, 5 March 1964; *Chem. Abstr.*, **62** (1965), 13400.
82. Mattei, I. V., Gtavis, F. J. & Lowell, J. A., *US Pat.* 3,269,859 (to Rohm & Haas Co.). 30 August 1966; *Belg. Pat.* 647,640, 9 November, 1964; *Chem. Abstr.*, 63 (1965), 8628.
83. Grief, M., *Leath. Mfr*, **81** (1964), 38.
84. Dolnick, A., *Leath. Mfr*, **82** (1965), 33.
85. Gardon, J. L., Lowell, J. A. & Porter, R., *Proceedings of the X Kongress of der Internationalen Union Der Gerberei — Chemikerverbande Luzern Schweiz* (Verein Schweizerischer Lederindustrie-Chemiker; Veslic; Walchestrasse 25, CH 8035 Zurich), 1967, 298.
86. May, M., *Leath. Sci.*, **16** (1969), 349.
87. Schiffers, F., *Aust. Leath. J.*, **71** (1969), 82.
88. Donath, G., *J. Soc. Leath. Trades Chem.*, **51** (1967), 58.
89. Zurabjan, K. N., *J. Soc. Leath. Trades Chem.*, **52** (1968), 306.
90. Reihsmann, R. M., *J. Am. Leath. Chem. Ass.*, **64** (1969), 101.
91. Arbaud, P., *Leather*, **172** (1970), 25.
92. Stahl, L., *Leath. Shoes*, **146** (1963), 16.
93. Neher, M. B. & Vely, V. G., *US Pat.* 3,066,997, 4 December 1962 (to Titekote Corp.); *Br. Pat.* 972,638; *Chem. Abstr.*, **58** (1963), 3623.
94. Neher, M. B. & Vely, V. G., *US Pat.* 3,261,655, 19 July 1966 (to Titekote Corp.), *Chem. Abstr.*, **65** (1966), 12435.
95. Neher, M. B. & Vely, V. G., *US Pat.* 3,261,656 (to Titekote Corp.), 19 July 1966; *Chem. Abstr.*, **65** (1966), 12436.
96. Lowell, J. A., Kroeker, E. H. & Buechler, P. R., *US Pat.* 3,231,420 (to Rohm & Haas Co.), 25 January 1966; *Belg. Pat.* 634,538, 6 January 1964; *Chem. Abstr.*, **61** (1964), 5923,
97. Boseden, G. A., *Leath. Mfr*, 78 (1961), 60.
98. Levy, E., *J. Soc. Leath. Trades Chem.*, 48 (1964), 122.
99. Donath, G., *Polyurethanes on leather*, paper presented at the Scientific Society of the Leather Shoe and Allied Industries, IV Congress, Budapest, Hungary, 14-18 Oct. 1970, Section Leather.
100. Pastuska, G., *Proceedings of the X Kongress of der internationalen union der gerberei-Chemiker verbande Luzern, Schweiz* (Verein Schweizericher Lederindustrie Chemiker, Walchestrasse 25, CH 8035, Zurich), 1967.
101. Heit, R. J., *J. Am. Leath. Chem. Ass.*, **64** (1969), 553.
102. Luvisi, F. P., Hopkins, W. J., Naghski, J. & Filachione, E. M., *J. Am. Leath. Chem. Ass.*, **61** (1966), 585.
103. Hopkins, W. J., Luvisi, F. P. & Filachione, E. M., *J. Am. Leath. Chem. Ass.*, **62** (1967), 162.
104. Neher, M. B. & Gallgher, N. D., *J. Am. Leath. Chem. Ass.*, **59** (1964), 403.
105. Base, R. L. & Porter, M. R., *Waterproofing and water repellency*, edited by J. L. Moilliet (Elsevier Publishing Co. Ltd. Amsterdom), 1963.
106. Gilkey, J. W., *US Pat.* 2.884,393 (to Dow Corning Corp.), 28 April 1959; *Chem. Abstr.*, **53** (1959), 16572.
107. Gilkey, J. W., *US Pat.* 894,967 (to Dow Corning Corpn) 14 July 1959; *Chem. Abstr.*, **54** (1960), 946.
108. Pail, D. R., *Fr. Pat.* 1,383,331, (to Dow Corning Corpn), 24 December 1964; *Chem. Abstr.*, **63**1956), 11875.
109. Stroganov, N. V., Ovchinnikov, V. A. & Sankin, G. M., *USSR Pat.* 171,951, 22 June 1965; *Chem. Abstr.*, **63** (1965), 16628.
110. Maminov, E. K. & Voronkov, M. G., *Chem. Abstr.*, **51** (1957), 17216.
111. Maminov, E. K., *Chem. Abstr.*, **53** (1957), 3956.
112. Heidemann, E. & Reiss, W., *Leder*, **14** (1963); 110.
113. Glozic, V. B., Vukovic, J. & Rusan, Z., *Leder*, 9 (1958), 81.
114. Morgan, F. R., *J. Soc. Leath. Trades Chem.*, 46 (1962), 290.
115. Jorczak, J. S. & Fettes, E. M., *Ind. Engng Chem.*, 43 (1951), 324.
116. Cranker, K. R. & Jorczak, J. S., *J. Am. Leath. Chem. Ass.*, 47 (1952), 178.
117. Cranker, K. R., *Leath, Mfr.*, 73 (1956), 42.
118. Cranker, K. R., *Insulation*, 2 (1956), 7.
119. Gourlay, P., *Chem. Abstr.*, 47 (1953), 6165.
120. Briggs, P. S., *J. Soc. Leath. Trades Chem.*, **52** (1968), 296.
121. Vago, G. & Figuli, J., *Leath. Sci.*, **16** (1969), 83.
122. Sutermeister, E. & Browne, F. L., *Casein and its industrial applications* (Reinhold Publishing Co., New York), 1948, 354.
123. Landmann, A. W., *J. Soc. Leath. Trades Chem.*, **48** (1964), 251.
124. Svoboda, V., Spickova, J. & Markova, J., *Chem. Abstr.*, 65 (1966), 12288.
125. Khaudozhko, E. N. & Euseeva, V. I., *Chem. Abstr.*, 62 (1965), 5385.
126. Trakhteuberg, S. I., Korostyleva, R. N. & Shuter, L. M., *Chem. Abstr.*, 62 (1965), 6682.
127. Belohradsky, F., Kulhanek, M. & Blazek, L., *Czeck. Pat.* 87,983, 15 December 1958; *Chem. Abstr.*, 54 (1960), 5176.
128. Langmaier, F., *Chem. Abstr.*, 68 (1968), 3723.
129. Toshev, T. & Ribarov, E., *Chem. Abstr.*, **72** (1970), 4349.
130. Dann, J. R., Illingesworth, B. D. & Gates (Jr), J. W., *US Pat.* 2,831,767, 22 April 1958 (to Eastman Kodak Co.); *Chem. Abstr.*, **52** (1958), 13314.
131. Smith D. A. & Fowler (Jr), N. F., *US Pat.* 2,811,494 (to Eastman Kodak Co.), 29 October 1957; *Chem. Abstr.*, **52** (1958), 1820.
132. Shevchenke, M. L., Kuryatniksv, E. I. & Uspenskaya, I. G., *Chem. Abstr.*, 75 (1971), 89354.
133. Kenichi, E., Shoji, K., Tsuneo, W., *Japan Pat.* 7,112,448 (to Konishiroku Photo Industry Co. Ltd), March 1968; *Chem. Abstr.*, 75 (1971), 152504.
134. Svoboda, V., Novotony, V., Krul, Z. & Bartos, J., *Chem. Abstr.*, **73** (1970), 121576.
135. Trakhtenberg, S. I., Kovalyak, E. K. & Vizgert, R. V., *Chem. Abstr.*, **75** (1971), 64675.
136. Zheltova, A. V. & Baramboim, N. K., *Chem. Abstr.*, 75 (1971), 130787.
137. Kedaba, J., Ciziunaite, E. & Golsteinaite, Z., *Chem. Abstr.*, **70** (1969), 4902.
138. Zheltova, A. V. & Baramboim, N. K., *Chem. Abstr.*, 74 (1971), 42974.
139. Trakhtenberg, S. I., Kovalyuk, E. K., Korostyleva, R. N. & Shuter, L. M., *Chem. Abstr.*, **69** (1968), 28632.
140. Hicks, E., *Shellac* (Chemical Publishing Co. Inc., New York), 1961.
141. Misra, G. S. & Sengupta, S. C., *Encyclopedia of polymer science and technology*, Vol. 12 (Interscience Publishers Inc., New York), **19**; 419.
142. Sahu, T. & Misra, G. S., *Indian J. Technol.*, **4** (1966), 370.
143. Sahu, T. & Misra, G. S., *Indian J. Technol.*, **6** (1968), 371.
144. Sahu, T. & Misra, G. S., *Res. & Ind., New Delhi*, **13** (1968), 61.

145. Subramaniam, V. V., Saroja, S. & Nayudamma, Y., *Indian Pat.* 117,677, 28 March 1970.
146. Nayudamma, Y., Rajadurai, S. & Muthiah, P. L., *Leath. Sci.*, 11 (1964), 352.
147. Mhaskar, V. V., *Proceedings of the symposium on leather auxiliaries*, Central Leather Research Institute, Madras, 1958, 184.
148. Rama Iyer, G. S. & Nayudamma, Y., *Proceedings of the symposium on leather auxiliaries*, Central Leather Research Institute, Madras, 186.
149. Blackley, D. C., *High polymer Lattices* (Maclaren & Sons Ltd; London), 1966.
150. Brown, G. L., *J. Polym. Sci.*, 22 (1956), 423.
151. Protzman, T. F. & Brown, G. L., *J. appl. Polym., Sci.*, 4 (1960), 81.
152. Shaw, R., *Leath. & Shoes*, 140 (1960), 25.
153. Rao, J. B. & Nayudamma, Y., *Proceedings of the symposium on leather auxiliaries*, Central Leather Research Institute, Madras, 1958, 217.
154. Murthi, G. S. N., *Proceedings of the symposium on leather auxiliaries*, Central Leather Research Institute, Madras, 1958, 221.
155. Mudd, J. S., *Leather finishes* (Chemical Publishing Co. Inc., New York), 1939.
156. Naidus, H., Katz, G. & Potash, M., *J. Am. Leath. Chem. Ass.*, 51 (1956), 6.
157. Handscomb, J. A., *J. Soc. Leath. Trades Chem.*, 43 (1959), 237.
158. Nutt, W. O., *J. Soc. Leath. Trades Chem.*, 41 (1957), 189.
159. Nutt, W. O., *J. Soc. Leath. Trades Chem.*, 43 (1959), 197.
160. Nutt, W. O., *J. Soc. Leath. Trades Chem.*, 44 (1960), 519.
161. Spiers, C. H. & Burnett, J. P. W., *J. Soc. Leath. Trades Chem.*, 43 (1959), 38.
162. Landmann, A. W. & Mitton, R. G., *J. Soc. Leath. Trades Chem.*, 46 (1962), 90, 97.
163. Landmann, A. W., *J. Soc. Leath. Trades Chem.*, 47 (1963), 38.
164. Landmann, A. W., *J. Soc. Leath. Trades Chem.*, 48 (1964), 205.
165. Sharphouse, J. A. & Jalaluddin, K., *J. Soc. Leath. Trades Chem.*, 48 (1964), 215.
166. Landmann, A. W. & Sofia, A., *J. Soc. Leath. Trades Chem.*, 54 (1970), 3.
167. Strout, G., *Leath. Mfr.*, 81 (1964), 45.
168. Venkatachalam, P. S., *Leath. Sci.*, 17 (1970), 213.
169. Doraiswami, B. & Venkatachalam, P. S., *Leath. Sci.*, 16 (1969), 119.
170. Emil Ott, Spurlin, H. M. & Graffton, E. M. W., *Cellulose and cellulose derivatives*, Parts I-III (Interscience Publishers Inc., New York), 1954, 1955.
171. Bikales, N. M. & Segal, L., *Cellulose and cellulose derivatives*, Parts IV and V (Interscience Publishers Inc., New York), 1971.
172. Menon, U. A., *Proceedings of the symposium on leather auxiliaries*, Central Leather Research Institute, Madras, 1958, 227.
173. Schubert, R. & Wurtele, L., *Das Leder*, 18 (1969), 121.
174. Subramaniam, V. V., *Tanner*, 26 (1971), 255.
175. Malm, C. J. & Smith, H. L., *Ind. Engng Chem.*, 38 (1946), 937.
176. Jarrett, M. E. D., *J. Soc. Leath. Trades Chem.*, 47 (1963), 178.
177. Speicher, W., *J. Soc. Leath. Trades Chem.*, 45 (1961), 104.
178. Hampton, H. A., Hurd, R. & Shearing, H. J., *J. Oil Colour Chem. Ass.*, 43 (1960), 96.
179. Freeborn, A. S., *J. Oil Colour. Chem. Ass.*, 48 (1965), 539.
180. Mennicken, G., *J. Oil Colour. Chem. Ass.*, 49 (1966), 639.
181. Kershaw, R., *Paint Technol.*, 30 (1966), 14.
182. Arbaud, P., *Leath. Mfr*, 86 (1969), 49.
183. Arbaud, P., *Leather*, 173 (1971), 29.
184. Pulles, F., *Leather*, 174 (1972), 84.
185. Wynn, D. A. W. & Pickering, R. C., *J. Soc. Leath. Trades Chem.*, 55 (1971), 263.
186. Schroer, W., *Bayderm-Process*, paper presented at the IV Congress of the Scientific Soiety of the Leather, Shoe and Allied Industries, Budapest, 14-19 October 1970.
187. Paukner, W., *Influence of easy-case finish on leather properties*, paper presented at the XII Congress of the International Union of Leather Chemists Societies, Prague, 5-11 September 1971.
188. Hall E. F., *S.A.T.R.A. Bull.*, 14 (1970), 66.
189. Münch, V. N., *Properties and uses of polyurethane transfer foils for leather finishing*, paper presented at the XII Congress of the International Union of Leather Chemists Societies, Prague, 5-11 September 1971.
190. Haemisegger, H., *Leath. & Shoes*, 146 (1963), 28.
191. Wall, L. A., *Fluoropolymers* (Interscience John Wiley & Sons Inc., New York), 1972.
192. Parthasarathi, T. K. & Ganesan, A., *Proceedings of the symposium on leather auxiliaries*, Central Leather Research Institute, Madras, 1958- 217.
193. Arya, L., *Proceedings of the sixth tanners' get-together*, Central Leather Research Institute, Madras, 1971.
194. Cassella (Jr), V. J., *Leath. Mfr*, 89 (1972), 35.
195. *Leather*, 173 (1971), 49.
196. Chen, P. S., *The chemistry and technology of leather*, Vol. II, Ch. 27, edited by F. O'Flaherty, T. Roddy & R. M. Lollar (Reinhold Publishing Co., New York), 1958, 408.
197. Mellon, E. F., *The chemistry and technology of leather*. Vol. II, Ch. 17, edited by F. O'Flaherty, T. Roddy & R. M. Lollar (Reinhold Publishing Co., New York), 1958, 66.
198. Windus, W., *J. Am. Leath. Chem. Ass.*, 47 (1952), 87.
199. Van Vlimmeren, P. J., *J. Soc. Leath. Trades Chem.*, 47 (1963), 65.
200. Windus, W., Filachione, E. M. & Happich, W. F., *US Pat.* 2,992,879 (to US Dept of Agriculture), 18 July 1961; *Chem. Abstr.*, 57 (1962), 2379.
201. Windus, W., Filachione, E. M. & Happich, W. F., *US Pat.* 3,104,151 (to US Dept of Agriculture), 17 September 1963; *Chem. Abstr.*, 59 (1963), 14208.
202. Windus, W. & Happich, W. F., *J. Am. Leath. Chem. Ass.*, 58 (1963), 638.
203. Happich, M. L. & Windus, W., *J. Am. Leath. Chem. Ass.*, 65 (1970), 135.
204. Ranganathan, S., Bose, S. M. & Nayudamma, Y., *Bull. cent. Leath. Res. Inst., Madras*, 4 (1957), 127.
205. Ranganathan, S., Bose, S. M. & Nayudamma, Y., *Bull. cent. Leath. Res. Inst., Madras*, 5 (1958), 131.
206. Fischer, R. F. & Smith, C. W., *US Pat.* 3,080,281 (to Shell Internationale Research Maatschappij, New York), 5 March, 1963; *Br. Pat.* 91,9720; *Chem. Abstr.*, 59 (1963), 1490.
207. Windus, W. & Hanningan, M. V., *J. Am. Leath. Chem. Ass.*, 60 (1965), 581.
208. Windus, W. & Hanningan, M. V., *US Pat.* 3,1,89,403 (to US Dept of Agriculture) 15 June 1965; *Chem. Abstr.*, 63 (1965), 8628.
209. Kuntzel, A., *Osterr, Leder Z.*, Festival No. D. 27-8 (1954).
210. Winheim, A. H. & Doherty, E., *J. Am. Leath. Chem. Ass.*, 45 (1950), 122.
211. Seligsberger, L. & Sadlier, C., *J. Am. Leath. Chem. Ass.*, 52 (1957), 2.
212. Fein, M. L. & Filachione, E. M., *J. Am. Leath. Chem. Ass.*, 52 (1957), 17.
213. Filachione, E. M., Fein, M. L. & Hains, E. H., *J. Am. Leath. Chem. Ass.*, 59 (1964), 281.
214. Filachione, E. M., Harris, E. H. & Fein, M. L., Korn, A. H. & Naghski, J. & Wells, P. A., *J. Am. Leath. Chem. Ass.*, 53 (1958), 77.
215. Filachione, E. M., *Leath. Mfr*, 77 (1960). 14.
216. Nayudamma, Y., Thomas Joseph, K. & Bose, S. M., *J. Am. Leath. Chem. Ass.*, 56 (1961), 548.
217. Nayudamma, Y., Hemalatha, R. & Thomas Joseph, K., *J. Am. Leath. Chem. Ass.*, 64 (1969), 444.
218. Chirita, G. & Chisalita, D., *J. Am. Leath. Chem. Ass.*, 66 (1971), 369.
219. Nayudamma, Y., Joseph, K. T., Panduranga Rao, K. & Hemalatha, R., *Leath, Sci.*, 14 (1967), 363.
220. Porter, R. & Davis, W. J., *Leather*, 171 (1969), 93.
221. Jean, N. & Pierre, G., *Ger. Pat.* 1,930,225 (to Pro gils A.), 19 February 1970; *Chem. Abstr.*, 72 (1970), 101874.
222. *Brit. Pat.* 1,111,868; *Neth. Pat.* 6,515,574 (to Rohm & Haas Co.), 2 December 1965; *Chem. Abstr.*, 65 (1966), 17222.
223. Kirk, J. S., *US Pat.* 2,452,536 (to E.I. du Pont de Nomours & Co.), 2 November 1948; *Chem. Abstr.*, 43 (1949), 1592.
224. Goebel, M. J., *US Pat.* 2,475,886, (to E.I. du Pont de Nemours & Co.) 12 July 1949; *Chem. Abstr.*, 43 (1949), 7738.
225. Batzer, H. & Grunewald, H. J., *Makromol. Chem.*, 9 (1953), 116.

226. Hermann, B., Erich, F. & Klaus, W., *Ger. Pat.* 1,278,677, 26 September 1968; *Chem. Abstr.*, **70** (1969), 48646.
227. Fischer, E., *Ger. Pat.* 1,281,094, 24 October 1968; *Chem. Abstr.*, **70** (1969), 21025.
228. Banderet, A., Scheibling, G. & Meng, J., *Chem. Abstr.*, **70** (1969), 97974.
229. Sykes, R. L., *J. Soc. Leath. Trades Chem.*, **41** (1957), 199.
230. Filachione, E. M. & Harris, E. H., *J. Am. Leath. Chem. Ass.*, **51** (1956), 160.
231. Clarke, I. D., Harris, E. H. & Filachione, E. M., *J. Am. Leath. Chem. Ass.*, **51** (1956), 574.
232. Vasantharaj, C. D. & Jayaraman, K. S., *Leath. Sci.*, **14** (1967), 186.
233. Putnam, R. C., *US Pat.* 2,523,326 (to United Shoe Machinery Corp.), 26 September 1950; *Chem. Abstr.*, **45** (1951), 378.
234. Bortnick, N. M., *US Pat.* 2,718,516 (to Rohm & Haas Co.), 20 September 1955; *Chem. Abstr.*, **50** (1956), 1371.
235. Young, H. H. & Christopher, E. F., *US Pat.* 2,816,099 (to Swift & Co.), 2 February 1960; *Chem. Abstr.*, **54** (1958), 5867.
236. Hans, E. & Friedrich, F. M., *Ger. Pat.* 1,945,005 (to Badische Anilin-und Soda-Fabrik AG), 11 March 1971; *Chem. Abstr.*, **74** (1971), 127581.
237. Guenther, E., Heinrich, H., Manfred, R. & Hans, E., *Ger. Pat.* 2,013,822 (to Badische Anilin-und Soda Fabric AG), 23 March 1970; *Chem. Abstr.*, **76** (1972), 5442.
238. Ramaswamy, D., Kedlaya, K. J., Jayaraman, K. S. & Satish Babu, K., *Leath. Sci.*, **19** (1972), 286.
239. Olivannan, M. S. & Nayudamma, Y., *J. scient. ind. Res.*, **28** (1969), 293.
240. Battaerd, H. A. J. & Tregear, G. W., *Graft copolymers* (Interscience Publishers, New York), 1967.
241. Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., *Leath. Sci.*, **14** (1967), 73.
242. Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., *Leder*, **19** (1968), 77.
243. Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., *Leath. Sci.*, **16** (1969), 401.
244. Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., *J. Polym. Sci.*, **9** (A-1) (1971), 3199.
245. Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., *J. appl. Polym. Sci.*, **16** (1972), 975.
246. Nayudamma, Y., Panduranga Rao, K. & Joseph, K. T., *Kozarstvi*, **22** (1972), 36.
247. Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., *Leath. Sci.*, **19** (1972), 27.
248. Panduranga Rao, K., Thomas Joseph, K., Kamat, D. H., Nayudamma, Y. & Sarkar, K. T., *Indian Pat.* 205/72 (filed).
249. Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., *Makromol. Chem.*, (in press).
250. Panduranga Rao, K., Thomas Joseph, K., Kamat, D. H., Sarkar, K. T. & Nayudamma, Y., (unpublished data).
251. Studniarski, K. & Hankiewicz, J., *Graft polymerization of vinyl monomers on collagen*, paper presented at the IV Congress of Scientific Society of the Leather, Shoe and Allied Industries, Budapest, 14-18 October 1970.
252. Kudaba, J. & Ciziunaite, E., *Chem. Abstr.*, **68** (1968), 78969; **70** (1969), 121225.
253. Jakubenaite, V., Kudaba, J. & Ciziunaite, E., *Chem. Abstr.*, **73** (1970), 4978.
254. Kudaba, J., Ciziunaite, E. & Mikelionyte, A., *Chem. Abstr.*, **73** (1970), 4980.
255. Kudaba, J. & Ciziunaite, E., *Chem. Abstr.*, **72** (1970), 32428.
256. Kudaba, J., Ciziunaite, E. & Jakubenaite, V., *Chem. Abstr.*, **74** (1971), 142706; **74** (1971), 32276.
257. Kudaba, J., Ciziunaite, E. & Jakubenaite, V., *Chem. Abstr.*, **75** (1971), 89087.
258. Korn, A. H., Feairheller, S. H. & Filachione, E. M., *J. Am. Leath. Chem. Ass.*, **67** (1972), 111.
259. Panduranga Rao, K., Thomas, Joseph, K. & Nayudamma, Y., *J. scient. ind. Res.*, **29** (1970), 559.
260. Panduranga Rao, K., *The preparation and determination of the physicochemical properties of chemically modified collagen*, Ph.D. thesis, Madras University, 1970.
261. Panduranga Rao, K., Thomas Joseph, K. & Nayudamma, Y., *Leath. Sci.*, **21** (1974), 35.
262. Payne, A. R., *Poromerics in the shoe industry* (Elsevier Publishing Co. Ltd, Amsterdam), 1970.
263. Keech, B., *Leath. Sci.*, **17** (1970), 236.
264. Kamat, D. H., *Leath. Sci.*, **17** (1970), 274.
265. Beck, P. J. & Lhuede, E. P., *Aust. Leath. J.*, **75** (1972), 20.
266. Moore, W. R., *J. Soc. Leath. Trades Chem.*, **50** (1966), 94.
267. Turner, R. H., *J. Indian Leath. Tech. Ass.*, **19** (1971), 8.