

Structure and Properties of Natural and Artificial Leathers*

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The Scanning Electron Microscope (SEM) has been used to determine the structure and to study the mechanical and chemical stability of natural and artificial leathers in wear and after testing in the laboratory. Artificial leathers, such as impermeable coated fabrics and poromerics which are permeable to water vapour, have been used more frequently in the last decade for clothing and footwear.

The mechanical flex cracking of leather and poromerics is discussed and the SEM studies have enabled the type of failure of the material in laboratory tests to be compared with that found in worn footwear.

Recent work has demonstrated that chemical degradation of poromerics is due to hydrolysis of the polyurethane used in the microporous layer and these results have been confirmed by SEM studies. Reasonably good correlation between laboratory hydrolysis tests and chemical deterioration of the poromerics in wear has also been found.

1. Introduction

The use of artificial leathers such as poromerics and coated fabrics in clothing and footwear has grown widely during the past decade. These materials are very different in structure and chemical constitution to the fibrous natural product and consist of various combinations of solid, cellular or foam polymers usually with a textile (knitted, woven and/or non-woven) base.

The introduction of these new materials has necessitated the investigation of the relationship between the structure and the properties exhibited by artificial and natural leathers in general and of the relationship between their behaviour in wear and in laboratory testing. Up to the present, this information has been obtained either by physical measurement or optical microscopy; however, information which required detailed visual inspection of natural or artificial leather was difficult to obtain.

The large depth of focus, ease of sample preparation, high magnification and resolving power offered by the scanning electron microscope has led to a number of investigations into the structure of polymers [1, 2] textiles [2-5] and foam [6] materials. Artificial leathers, however, are a combination of these three types of

structure and have up to the present, received little investigation [7] by this technique.

This paper describes how the scanning electron microscope (SEM) has been used to study the structure of natural and artificial leathers and to investigate the mechanical and chemical stability of these materials both in wear and in laboratory testing.

2. Experimental Details

Samples of natural and artificial leathers were cut by a razor blade (the modern coated stainless steel type is excellent for this purpose) both from laboratory samples and from worn shoes. The samples were then mounted by use of an adhesive on an SEM stub in the usual way. The dimensions of the samples were in general about 5×2 mm and three or four specimens could be conveniently placed on one stub.

Natural and artificial leathers are poor electrical-conductors and it is usually necessary to coat them with a thin layer of metal in a vacuum evaporator. Several methods have been tried with varying success, the major aim being to provide a surface coating which is sufficiently conductive to discharge from the sample surface any static charges which are built up by the

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scanning electron beam. However, the metal coating must not be so thick that it masks surface detail. The best results were obtained by applying a base coating of carbon followed by one of gold/palladium. The total thickness of the coating was about 500 Å. The SEM was operated in all cases at 20 KeV and the angle of tilt of the specimens was either 0 or 45°. The photomicrographs shown in this paper were obtained on the "Stereoscan" microscope at Cambridge Scientific Instruments Ltd.

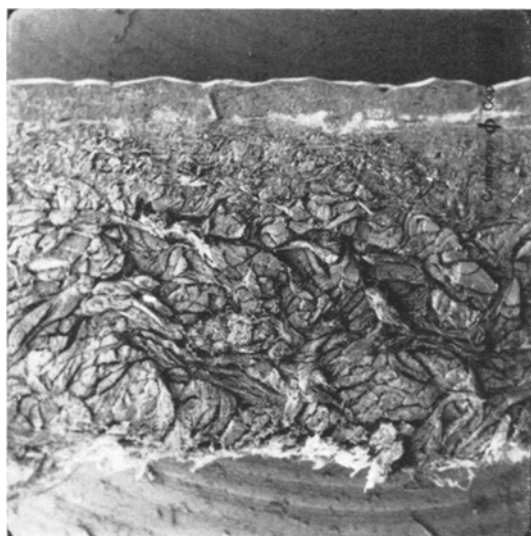


Figure 1 Cross-section of side leather.

The coarse meaty fibres are typical of the corium region of leather, these coarse fibres are made up of bundles of the main leather fibres. The fibre bundles become progressively very much finer nearer to the grain surface. Due to loss of protein material during the preliminary stages of the tanning process, and sometimes due to microbiological deterioration before tanning, the region between the top tightly-packed grain layer and the next "thermal" layer of intermediate fibre size loses cohesion and some delamination can occur. There are some signs of localised delamination in this specimen.

The fibre bundles are very densely packed and there are no voids with relatively large dimensions such as occur in porous artificial leathers. No binder material is present in leather, the cohesion between fibre bundles and fibres depending upon more subtle effects such as interweaving, and chemically based surface attractive forces ($\times 25$).

3. The Structure of Leatherlike Materials

3.1. Natural Leather

The typical structure of natural leather is shown in fig. 1; this is a cross-section of a sample of side leather*. The characteristic tightly packed fibre system is very apparent and the photograph

shows the absence of large voids (a large proportion of void spaces is characteristic of artificial leather) and the gradation in fibre size from coarse fibres in the flesh and corium (central) regions, to the much finer fibrous structure found in the grain (outersurface) region. A further unique feature of leather is the absence of any form of binder material between the fibres, still an essential component of artificial leathers; this is probably the reason why it has such excellent flexing, tensile and handle properties and has been found to be a first class material for footwear for very many generations.

Despite leather's excellence for the manufacture of footwear, gloves, clothing and upholstery and for certain engineering applications it does suffer from some serious disadvantages. For example, it cannot be obtained in uniform rolls and this has delayed automation in these industries. Also, serious faults within leather are caused by insects such as warble fly whose larvae live in the animal skin. Fungal infections, e.g. ringworm, can also cause damage as do

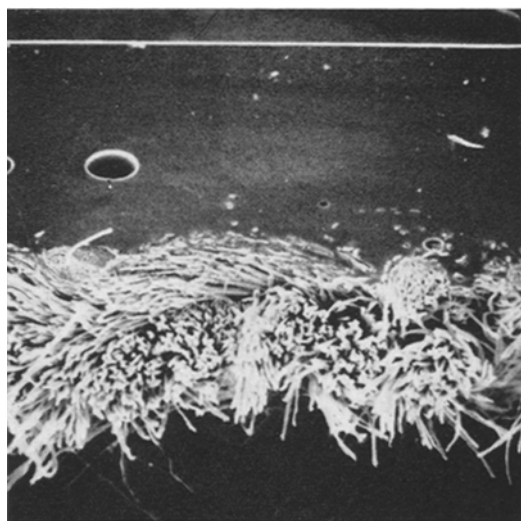


Figure 2 Cross-section of solid PVC skin on woven base.

This is the simplest type of coated woven fabric and penetration of the polymer into the top regions of the fabric weave shows that the material was coated directly with the PVC plastisol. Over-penetration of the PVC must be avoided because it has an adverse effect upon the fabric properties. The few voids in the polymer layer are due to air inclusions during coating. Where the polymer layer consists of two or more layers, and this is not uncommon, metallisation of the specimen can sometimes hide the junctions and give a false indication of a single layer coating ($\times 32$).

*Calves and young oxen provide calf leather whilst the hides of older and larger oxen are cut into halves along the backbone, i.e. into sides. Calf leather is left untouched but because of skin defects in older animals side leather is sanded, thus much of the fine grain layer is removed.

scratches from barbed wire fences. Variations in leather quality are also imposed by the interaction of many biological factors. These variations have to be masked by the tanner as best he can. It is mainly for these reasons that synthetic materials have emerged as competitive alternatives to the natural product.

3.2. Artificial Leather

3.2.1. Coated Fabrics

The first group of man-made upper materials to be used by the footwear industry were impermeable plastic-coated fabrics. There are very many types of coated fabrics [8], but the materials used most frequently in the footwear industry are solid or expanded polyvinylchloride (PVC), supported upon a woven, knitted or impregnated non-woven fabric base. The fibres most widely used for the base fabric are cotton and nylon. A number of these materials have been examined in the SEM. Fig. 2 shows a thick solid PVC coating on a woven base and fig. 3 a cellular PVC on a non-woven base. Combinations of these structures can occur, see fig. 4, with both solid and cellular PVC supported by a woven base.

The plastic coating on the fabric provides the

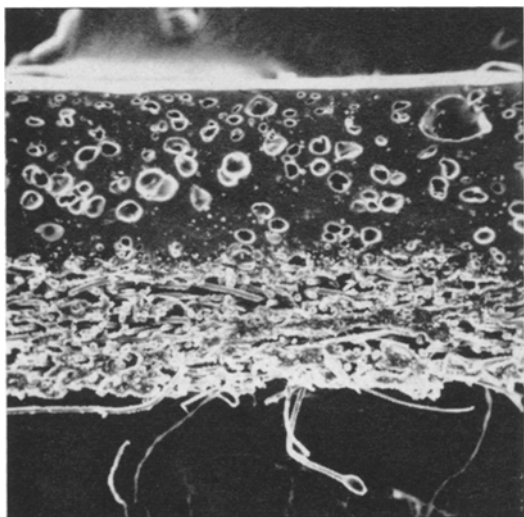


Figure 3 Cross-section of cellular PVC on non-woven base.

This is an impermeable upper material ("QUOX"), hence the low proportion of voids in the PVC. The plastisol has been directly coated onto the non-woven substrate as shown by penetration into the uneven surface. The surface reticulation on some of the fibres in the non-woven layer can be clearly seen, also the solid neoprene binder. This latter is not uniformly distributed and appears to have formed into layers within the non-woven structure ($\times 28$).

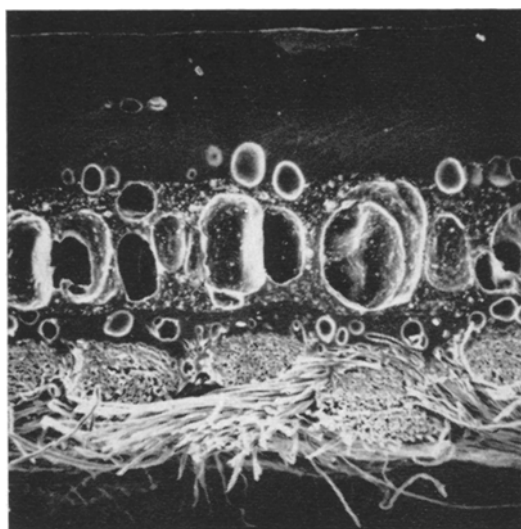


Figure 4 Cross-section of solid and cellular PVC on woven cotton base.

The three layers of this polymer structure which can be clearly seen, have been direct-coated. The foam interlayer, which has uncommonly large cells, lies upon a relatively thin key layer, this latter having impregnated between the threads of the fabric. The top solid film is about half the total thickness of the whole polymer layer, which provides a tough abrasion resistant surface. This material is used in men's shoes and the interplay of the very different physical properties of the different layers can cause breakdown of the cellular layer thus causing delamination ($\times 25$).

attractive finish, which can be coloured, printed and embossed to provide many varied effects, but is usually required to be leatherlike. It provides the good wearing properties of the product, and it must be able to withstand a considerable amount of abrasion and flexing and retain a good appearance. The nature of the polymer coating affects the handle of the product, in that the coating may be stiff and harsh, or soft and supple, according to requirements. The fabric provides most of the tensile strength and almost the whole of the tear strength of the product. The fabric also considerably modifies the stretch properties of the coating and makes a major contribution to the handle of the material. Interaction effects between plastic and fabric are pronounced, e.g. tear strength of the composite may be less than that of the strongest component, but the scientific study of the properties of flexible composites has been limited.

The major problem with PVC-coated fabric materials is that in most cases they are impermeable and thus prevent sweat escaping. The sweat materials accumulate at the junction between the coating and the fabric and can cause delamination. Microporous PVC coatings have been

developed which are permeable to water vapour, but they suffer from poor surface abrasion properties and are at present limited to use as footwear linings.

3.2.2. Poromerics

The development of a synthetic leatherlike material having moisture absorption and permeability properties similar to natural leather was started in 1936 by E. I. du Pont de Neumours Inc, USA, but it was not until the early 1960s that their product known as "Corfam" appeared in Britain and they were the first to use the term *poromeric* to describe such materials. Since then several poromeric materials of widely differing structures [9, 10] have been produced and marketed; some of the results of SEM studies on these materials are presented in this paper.

Most of the developments of poromerics have been based upon an attempt to imitate the fibrous structure of leather, and in several cases leather fibres have been used in the formulations.

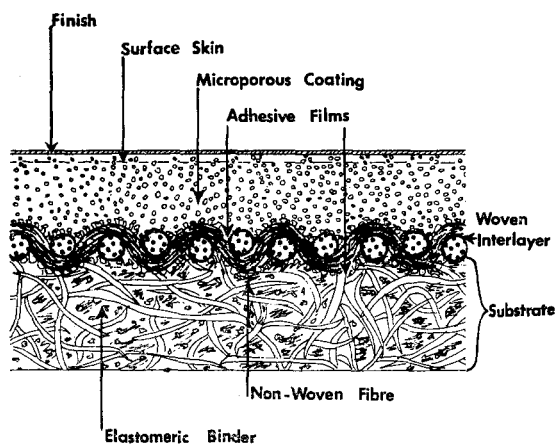


Figure 5 Diagrammatic representation of the structure of typical poromerics.

An indication of the various components in a multilayer poromeric is given in fig. 5. This use of a fibrous substrate has led to considerable investigation and development of the technology of non-woven fabrics and their impregnation with elastomeric polymers. Indeed, it is probably true to say that the substrates of fibrous poromerics represent the most sophisticated and advanced forms of non-woven fabric technology in the world today. This is especially true of the high fibre density, random structure type exemplified by the Corfam substrate shown in fig. 6.

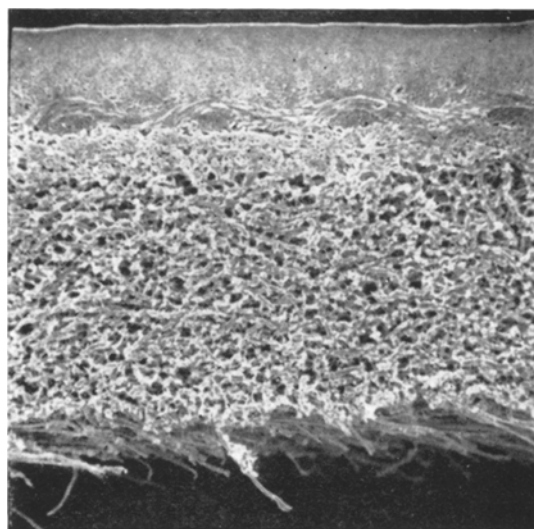


Figure 6 Cross-section of "Corfam" poromeric.

The microporous top layer is separated by a woven fabric interlayer of Dacron from the non-woven substrate. The microporous layer has relatively large cells next to the interlayer decreasing in size towards the surface, which is solid but permeable to water vapour. The packing density of the fibres in the non-woven substrate is very high as is the degree of randomness, although the distribution of fibres is uniform. The amount of binder appears to be uncommonly small for a man-made material but note the large amount of binder next to the Dacron interlayer ($\times 35$).

3.3. Poromeric Structures

Poromerics in general have at least two discrete layers and some of the fibrous types such as Corfam, shown in fig. 6 may have as many as five layers.

The layers are:

(a) *Finish (or top) layer*. This is a very thin film (about 0.005 mm thick) applied to the otherwise complete poromeric. These finishes are commonly acrylic polymers but may sometimes be transparent polyurethane.

(b) *Surface skin*. This is usually an integral part of the microporous layer, being formed as a result of fusion of the outermost cells. In some cases this surface skin is formed during a film release process and in others as part of the grain embossing process. The thickness (usually about 0.01-0.04 mm) and properties of this skin are very important because they affect the liquid water (resistance to water penetration) and water vapour permeabilities of the poromeric, also resistance to scuffing and snagging damage; also, in combination with the microporous coating, they determine the type of "break" (wrinkle formation) that the material will form when folded.

(c) *Microporous layer.* The thickness of the combined surface skin plus microporous layer varies with the different commercial materials [11]. The microporous layer is generally a permeable foam of small cell dimensions, although several different types of cellular structures are employed in different materials.

Water vapour transport through the foam probably consists of three mechanisms [12, 13].

(i) Diffusion through the interconnecting voids as a result of the thermal and water vapour concentration gradients across the material.

(ii) Water absorption-desorption along the surfaces of the cell walls.

(iii) Transmission through the polyurethane cell walls. The water absorption capacity of the polyurethane probably has a large influence on these moisture transmission properties and the development of polymers of high moisture absorptive capacity has recently led to absorption values of up to 300% [14].

(d) *The interlayer.* This is commonly a woven fabric which separates the microporous layer from the non-woven substrate in some materials. This component serves several purposes, e.g.:

(i) increases tensile and tear strength (but reduces breaking extension);

(ii) controls stretch and creep;

(iii) masks surface unevenness when the material is strained;

(iv) places the neutral plane of the material close to the surface skin.

The interlayer fabric is polyester in Corfam, but various fibres are used in different poromerics. Although such interlayers provide the benefits listed above, their use creates the problem of delamination which has caused some difficulties in shoe manufacture.

(e) *The substrate.* This can be a non-woven, woven or knitted fabric all of which are impregnated to various extents with a polyurethane elastomeric binder. In one case, discussed below, the substrate is cellular polyurethane only.

In general the impregnated substrates tend to behave like the fabric reinforcement which they contain, thus substrates with a non-woven matrix will have a high breaking extension and tend to creep, whereas those substrates with woven fabrics will have lower breaking extensions and will tend not to creep, knitted substrates come somewhere between the two. The manufacture of poromerics has been discussed in several recent publications [9, 15].

The five layers discussed above can be seen in

the case of Corfam shown in fig. 6. The density of fibres in this material is very much higher than in any other poromeric and approaches that found in natural leather. The polyurethane microporous layer in Corfam differs from most of the other poromerics in that it is based on a polyether polyurethane rather than a polyester. It has not so far been possible to differentiate between the different polymers in the SEM, although this may be possible in the future.

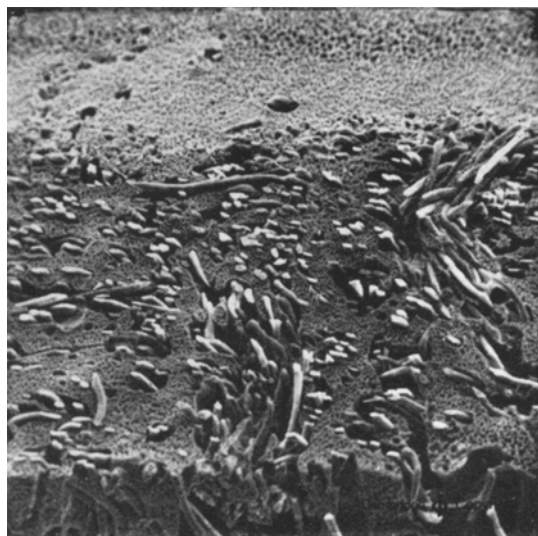


Figure 7 Cross-section of poromeric "Clarino".

This material is characterised by large bundles of fibres, caused by needling, in a matrix of polyurethane foam. The fibres pass through tunnels in the foam, these tunnels having a smooth closed surface, with no adhesion to or between fibres. This structure has a relatively low extension modulus, a valuable feature for comfortable footwear. The microporous top layer has rather larger voids than Corfam. The picture shows that the foam in the substrate is different to the top layer and has larger cells, the top layer having been applied by direct coating ($\times 63$).

Fig. 7 shows the structure of the poromeric Clarino which is characterised by the absence of an interlayer. The other major difference between Clarino and Corfam is the much larger amount of foam elastomer in the substrate. It can be clearly seen from the SEM photograph how little adhesion is apparent between the fibres and the foam, an interesting departure from the usual non-woven structure. It is this absence of adhesion which contributes to the relatively good handle properties of Clarino. The other significant feature in this connection is the small proportion of fibrous component in the substrate; it is much smaller in Clarino than in any

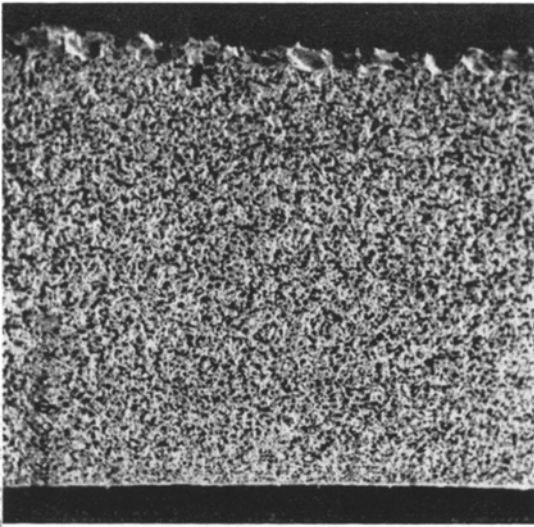


Figure 8 Cross-section of poromeric "Porvair".

The metallisation has masked what appears to be a two layer structure in this material. The cross-section of the untreated material shows a black layer of rather less than half the total thickness, lying on a thicker grey layer, however, close examination of the SEM picture does not indicate any demarcation line in the foam. An interesting feature of this material is the very thin top skin, much thinner than any other poromeric shoe material. This polymer foam is viscoelastic and has a relatively low extension modulus compared with leather and poromerics ($\times 35$).

other fibrous poromeric. The fibres in this material are nylon and viscose rayon.

Several poromerics have been examined with the SEM which are similar in structure to the materials shown in figs. 6 and 7. Recently a "second generation" of poromerics has appeared which consist of just a surface skin and micro-

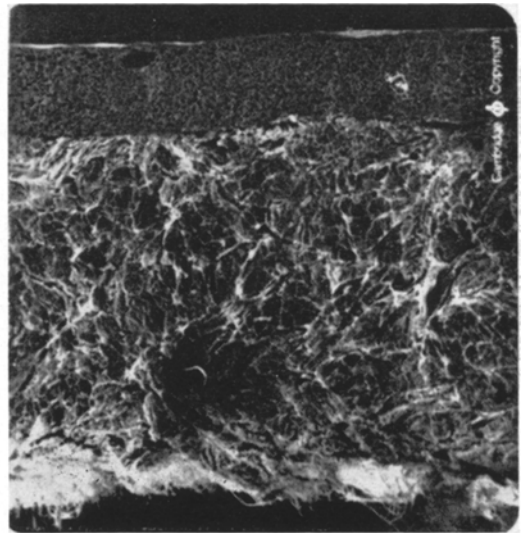


Figure 9 Cross-section of microporous polyurethane-coated leather.

The thick ox hides from older animals are usually split into two; a grain carrying layer and a cheaper flesh split. Recent attempts to find new outlets for these latter materials have taken the course of laminating permeable polyurethane microporous foams onto the leather split, i.e. the leather split is taking the place of the non-woven substrate in the poromerics. The foam is made using a release film process so that adhesion between leather and foam is probably less good than would result from a direct coating process. Some regions showing absence of contact between the two layers can be seen in this SEM photograph. The leather shows the typical coarse fibrous structure with no "thermal" or grain region. Materials such as this possess the desirable high water vapour absorption properties of leather - an asset for comfortable footwear ($\times 36$).

porous polyurethane foam as shown by the stereoscan photograph of "Porvair" in fig. 8. The modulus of this material is lower than in the case of the fibrous poromerics and it has good

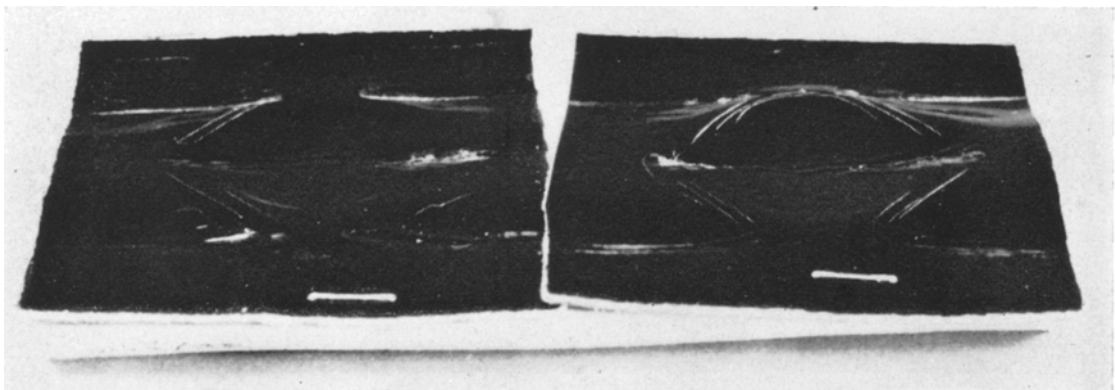


Figure 10 Type of flexing samples used in SATRA test (SEM 101).

This test simulates the type of diamond-shaped fold which appears on the front of shoe uppers during wear. Most man-made upper materials show failure due to cracks on the convex regions of the fold - this can be seen in this photograph. Surface strains can reach 40% linear strain on the top of the convex fold. A satisfactory shoe material should take one million flexes in this test with no sign of damage; many materials fail to reach this standard.

surface abrasion properties. The material is also different to the other poromerics in that it displays viscoelastic behaviour and behaves as a polymer with time-temperature-dependent physical properties. The breaking extension of the material is over 400%, which may be compared with values of under 100% for most of the fibre-based poromerics.

3.4. Combinations of Artificial and Natural Leathers: Collagenous Poromerics

In attempts to obtain the excellent moisture-absorptive and moisture-responsive properties of leather in poromerics, manufacturers have tried to produce artificial leather by use of either leather or collagen fibres as the raw materials. Two methods are generally used: in the first method leather fibres are reformed into fibrous sheets from comminuted leather scrap and in the second method untanned collagen is dissolved from the raw animal hide followed by reconstitution of the collagen fibres into fibrous webs, both by chemical processes. The resulting sheet material is then tanned and coated with a water vapour permeable polymer skin to produce the artificial leather.

As well as attempts to produce a roll of material from leather or collagen fibres, considerable effort has been applied to the production of easy-clean leathers which can compete with the artificial materials. One approach has been to coat natural leather with a polyurethane foam material as shown in fig. 9. The use of a microporous top layer has allowed the natural product to retain its permeability and absorption properties.

The demands of fashion have led to the coating of natural leathers with solid polyurethane finishes which add colour and improve the appearance of the natural product but reduces its permeability substantially. This has recently been apparent with the "wet look" vogue, and the coating of leather with an impermeable polymer has caused problems of delamination as discussed in the next section.

4. Deterioration in Service

4.1. Mechanical Flex-Cracking of Leather

One of the most important properties of leather, especially with regard to its use in shoes is that it displays good resistance to flex-cracking. The type of samples used in the SATRA flexing test [16] are shown in fig. 10. The flexing heads have been so designed that they simulate the flexing and

folding conditions which occur in wear. Surface strains of up to 40% are induced in the sample on the peaks of the convex folds. Good agreement has been found between this flexing test and the durability of the materials in wear. Average quality leather will generally flex several million times without cracking in this type of test; most of the man-made materials giving a much poorer performance.



Figure 11 Delamination of polyurethane coating on a "wet look" leather.

This is a so-called "wet look" leather made by coating leather with a thin film of solid polyurethane. The picture has been taken at the point of convex fold in a flexed specimen. As a result of the flexing forces the polymer film has delaminated, this leads to pronounced local folds in the film in the delaminated region. A crack has formed and propagated along the foot of the fold in the polymer film. The smooth surface of the leather seen in the delaminated region probably had an adverse effect upon the adhesion between the layers. Due to the low permeability of the polymer film, sweat can accumulate at the junction with the leather and this also can have a pronounced adverse effect on adhesion. PVC-coated leather shows a similar type of failure ($\times 126$).

Fig. 11 shows a cross-section of a polyurethane coated "wet look" leather after 20000 flexes on the SATRA machine. Delamination of the surface coating from the leather is clearly apparent. Irregularities in the leather surface have caused the polyurethane to impregnate the surface in isolated areas as shown by the extra thick coating in one place. This localised thickening of polyurethane may have contributed to the formation of a crack in this particular place, however the crack has appeared at the base of the concave fold induced in the sample during the flexing and it is more likely to be due

to high localised stresses resulting from the delamination. There is no indication of leather fibres being attached to the underside of the polyurethane coating and hence it can be concluded from this photograph that cracking and delamination is due to the poor adhesion of the surface coating to the leather. A large number of failures have occurred in practice in a similar way.

The flex-cracking resistance of the wet look leather in wear, however, is aggravated by the low permeability of the polyurethane coating. Hence, sweat escaping from the foot causes chemical attack upon the leather and possibly the adhesive at the junction of the finish and leather which increases the possibility of delamination under mechanical flexing.

A surface view of a sample of natural leather (carrying a thin acrylic finish layer) which has been flexed 20000 cycles is shown in fig. 12 and severe cracking of the finish is apparent. A cross-sectional view of the same sample is shown in fig. 13 and it can be seen that mechanical flexing has caused cracking and delamination of the surface finish away from the grain surface of the leather. This type of failure is aggravated by moisture coming into contact with the finish/leather interface.

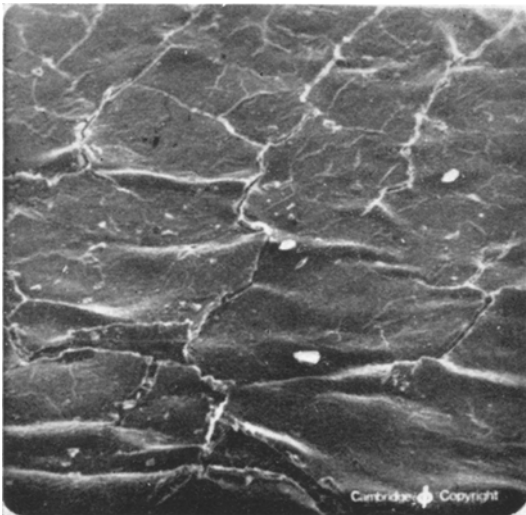


Figure 12 Surface of a grained natural leather after 20 000 flexes.

Leather is usually finished with a thin pigmented polymer film. These finishes are based upon nitrocellulose, acrylic or casein polymers and resistance to flexing is variable, with moisture having a pronounced effect in impairing the flex resistance of the film. The surface view photograph shows the typical crazing and delamination which takes place ($\times 63$).



Figure 13 Cross-section of grained natural leather after 20 000 flexes.

This shows a cross-section of the specimen described in fig. 12. The rough edges and appearance of the delaminated film suggests brittle failure of the material ($\times 63$).

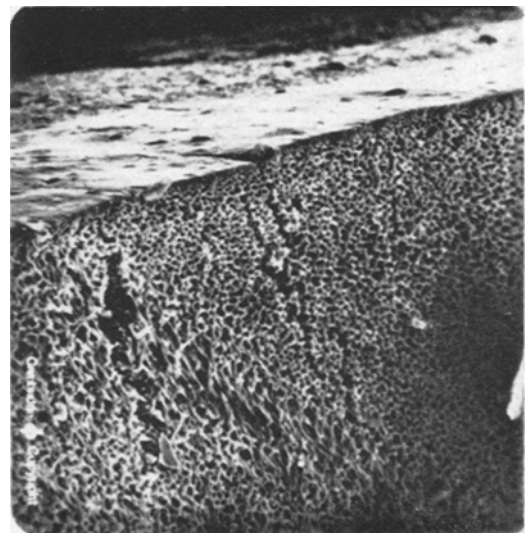


Figure 14 Cross-section of poromeric after 500 000 flexes. Sample from convex fold of test piece. Some surface damage from metallisation can be seen.

This is the microporous layer only and the photograph indicates that cracks form within the foam during flexing and propagate to the surface skin ($\times 147$).

4.2. Mechanical Flex-Cracking of Poromerics
Flex-cracking of the microporous polyurethane component is a problem with a number of poromerics and fig. 14 shows the type of damage that

occurs. This poromeric had been flexed for 500000 cycles on the SATRA flexing machine and several cracks through the cell structure can be clearly seen, although some of the cracks had not at that stage reached the surface. Also shown in this figure is a region of fused cells in the left-hand side of the photograph stretching through to the central base region. It is believed that this apparent fault in the cellular structure is an artifact resulting from the spluttering of metal particles during the coating of the sample.

An enlargement of the area where the crack propagates through the surface skin of the poromeric in fig. 14 is shown in fig. 15. The photograph shows some delamination of the surface finish and it can be seen that the crack has propagated by cell wall breakdown.

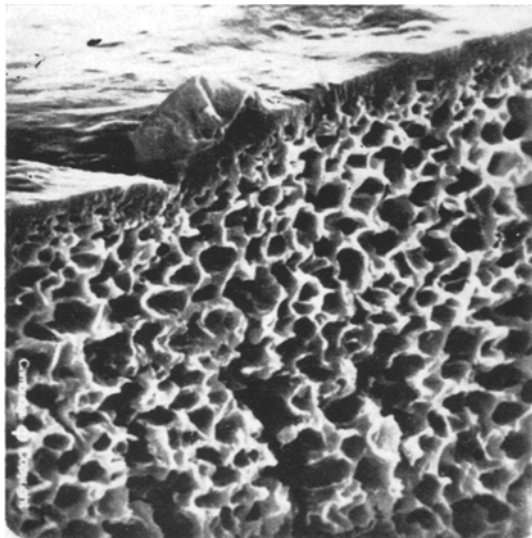


Figure 15 Enlarged view of crack in poromeric shown in fig. 14 propagating through surface.

Poromerics are also finished with thin films of lacquer and delamination of this very thin film can be seen in this photograph. Damage in the foam appears to be simple mechanical cell wall failure ($\times 735$).

An example of the type of mechanical failure that occurs in footwear is shown in fig. 16 which is a sample taken from the central crease in the front of a poromeric shoe upper after a period of wear. Cracks have propagated in a similar manner to the cracks shown in the laboratory flexed samples and have in the case of this particular shoe propagated not only through to the surface of the poromeric, but also at 90° to the original crack to cause weakness along a line

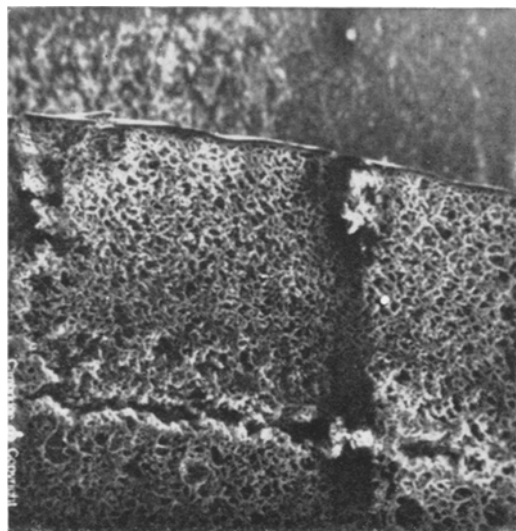


Figure 16 Sample taken from front of poromeric shoe showing mechanical failure.

The crack has propagated through the microporous layer and along the junction between the two foam layers. Other photographs show that the laminar failure is in the region of a third thin foam layer, the crack having propagated along the lower junction of this thin foam with the main substrate ($\times 70$).

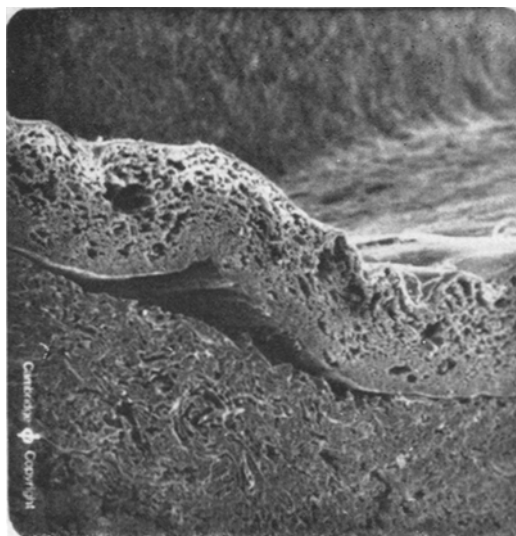


Figure 17 Sample from worn poromeric shoe showing serious delamination of surface.

This SEM photograph demonstrates the delamination which can occur with poromeric and other materials made by the transfer coating process. The high density surface in the microporous layer could be expected to apply relatively strong normal and plane forces to the junction during flexing. The photograph shows that adhesion is not good in regions away from the delaminated area. The wrinkles on the junction surface of the top layer no doubt contribute to the delaminating forces ($\times 95$).

of cells parallel to the surface skin. This would eventually lead to delamination of the surface layer. It is interesting to note in this particular poromeric that the crack has propagated along a line of cells parallel to the surface which are different in size to those of either side of the crack. This position coincides with the interface of two foam layers, one having been coated onto the other. These two foams were known to have different mechanical properties, e.g. modulus.

Serious delamination of the microporous surface layer from the substrate can occur in certain poromerics when in wear as shown by the photograph in fig. 17. This is also a sample taken from the crease in the front part of a shoe upper. The microporous layer has been permanently distorted as shown by the SEM photograph. This material is an example of the transfer coating process in which the microporous layer is formed upon a release film and is subsequently attached to the substrate as a ready-made layer requiring an adhesive for attachment to the substrate. Laminated systems such as this appear to be susceptible to mechanical and chemical deterioration at the interface to a greater extent than direct-coated substrates.

It is necessary for a natural or artificial leather which is to be used as an upper material in shoes, to have good folding properties. The way in which folds form can greatly effect the comfort of the shoe, its resistance to flex cracking and the general appearance. A limited study using the SEM has been done to investigate folding characteristics of upper material. An example of wrinkling and folding in an artificial leather is shown in fig. 18. This is a sample which had been chemically degraded in the laboratory to about 50% of its original strength. The folds are very well rounded and would be quite acceptable on the front of a shoe. An enlargement, however, of the base of one of the folds in fig. 19 shows a crack propagating inwards from the surface of the outer skin. The pronounced crease induced in the material in this region has created a stress concentration at the surface which has initiated a flaw; this then propagating through the outer skin of the poromeric as a result of continuous flexing.

4.3. Chemical Degradation of Poromerics

Chemical degradation by foot sweat which has led to failure of natural leather used in shoe uppers has been a problem for many years due to the hardening and cracking of the surface



Figure 18 Folding characteristics of poromeric degraded to 50% of its original tensile energy ($\times 70$).

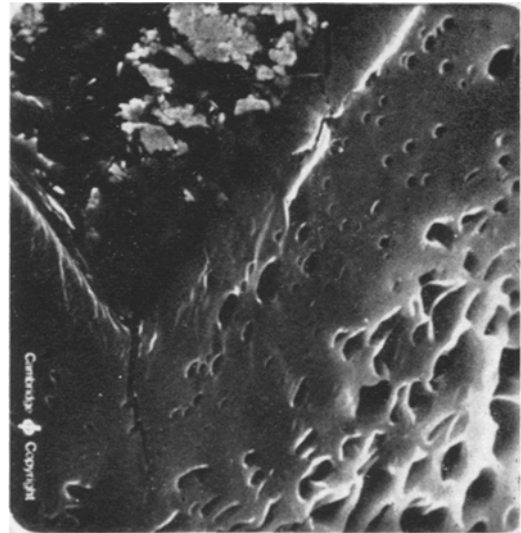


Figure 19 Close-up of one of the folds shown in fig. 18 showing crack formation and propagation in the surface skin of the microporous layer.

The sample has been flexed 25 000 times after steam degradation. The wrinkles have been permanently set and the formation of a crack in the surface skin at the bottom of one of the wrinkles can be seen ($\times 1400$).

associated with detannage of the leather by the lactate present in sweat. It has been found recently that some polyurethane-based poromerics are also attacked by human sweat [17], leading in the case of some urethane polymers,

to severe and fairly rapid deterioration during wear.

As a result of chemical degradation in poromerics, the microporous layer usually becomes brittle and loses its elasticity and flexibility. Cracks appear where the material is extended or flexed and soon afterwards delamination occurs with the microporous layer breaking away from the substrate. The effects found in poromeric shoe uppers during wear are shown in fig. 20. The significant feature which points to chemical degradation during wear is that delamination of the microporous layer has occurred at pressure points of the foot against the shoe upper, thus allowing direct transfer of sweat from the foot. The SEM has provided a very useful tool in examining chemical degradation of this type in artificial leather composites.



Figure 20 Poromeric shoe upper showing damaged microporous layer due to chemical degradation.

The degraded microporous polyurethane top layer has broken away from the non-woven substrate.

A typical example of chemical degradation in a poromeric shoe during wear is shown in the SEM photograph in fig. 21. A number of cracks have appeared in the microporous layer but only a few have penetrated to the surface. In some regions a number of the cracks have united to produce a crumbling of the polyurethane foam although the surface skin has remained fairly intact. A close-up of a typical crack from the microporous layer of the poromeric in fig. 21 is shown in fig. 22. The crack has propagated by simple cell breakdown and there is little sign that the cells around the crack have fused due to chemical degradation of the poromeric caused by sweat from the foot.

Recent work [17] has demonstrated that the



Figure 21 Sample of poromeric shoe upper with severe cracking in microporous layer due to degradation by sweat.

Pronounced deterioration has taken place within the foam whilst the surface skin has remained intact in places. Due to thermal gradients sweat condenses in this microporous region especially in the case of heavy sweaters. Sweat is known to catalyse the hydrolysis reaction of polyurethanes and thus internal failure would be expected initially. There is extensive crumbling of the foam in this specimen ($\times 74$).

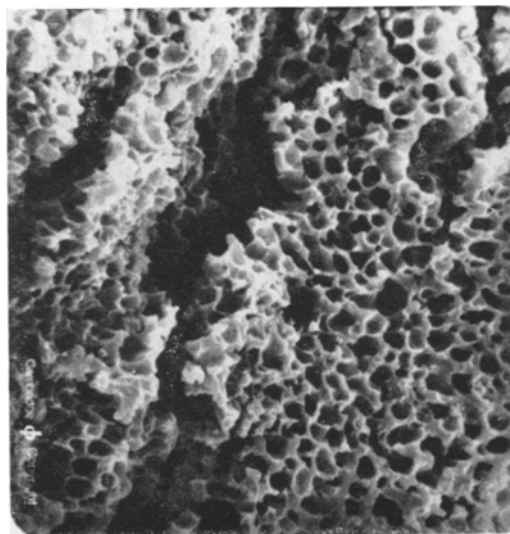


Figure 22 Close-up of one of cracks shown in fig. 21.

Cell wall failure appears to be brittle in type and there is little or no indication of the compression observed in foams which have been severely degraded under laboratory conditions (See fig. 26) ($\times 735$).

chemical degradation of commercial poromerics is due to hydrolysis of the polyurethane used in the microporous layer. Apparent activation

energies for polymer scission of between 12 to 20 kcal/mole are not uncommon and some wearers can degrade and embrittle such polymers in 6 to 10 weeks. Using time-temperature superposition methods it has been possible to predict the lifetime of various polymers when hydrolysed by distilled water, the type of master curve obtained from this work being shown in fig. 23.

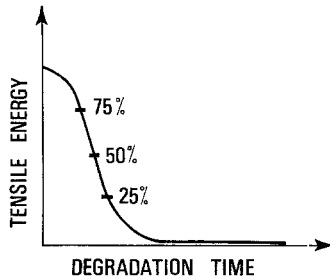


Figure 23 Controlled degradation of polyurethane foams.

This has been investigated using tensile energy measurements as an indication of degree of degradation. This shows a typical degradation curve for a foam treated with steam at 120° C for up to 24 h. The figures indicate the percentage of original strength remaining after various treatment times and samples degraded to these levels have been examined in the SEM.

Tensile energy measurements have been used in the superposition experiments, but it has also been shown that the molecular weight of a particular polyurethane in a poromeric is halved after 64 h immersion at 90° C in water. The addition of 1.2 gpl of urea caused the molecular weight to fall by nearly 70% under the same time and temperature conditions. The addition of sweat components (e.g. urea, ammonia) at the concentrations which occur in sweat, catalyses the degradation reaction(s) and activation energies are much reduced, as are the predicted lifetimes to given levels of degradation when these materials are present.

Samples of poromerics which have been degraded in laboratory hydrolysis tests to 75 and 25% of their original tensile energy have been examined by the SEM. The sample shown in fig. 24 has been degraded to 75% of its initial tensile energy to break, and then flexed 20000 cycles on the SATRA flexing machine. A large number of internal cracks have appeared in the microporous layer, the majority of which have not reached the surface of the poromeric. A similar sample flexed for the same number of cycles but without any prior degradation treatment, showed no internal cracks. The same poromeric was also subjected to a more severe

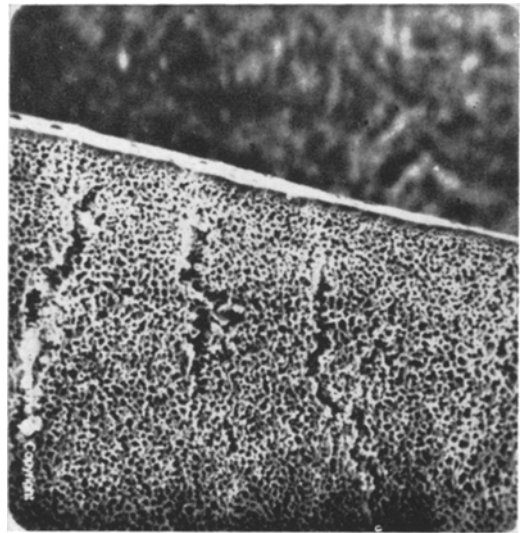


Figure 24 Cracking in microporous layer after degradation in steam at 120° C to 75% of its original tensile energy. After reconditioning (65% r.h./20° C) the specimen was flexed 20 000 times in the SATRA flexing machine.

Notice that failure has occurred in the cell structure only, and also the difference in polymer thickness between surface skin which is much thicker than the cell walls. Water diffusion rate in the polymer is probably an important parameter in hydrolysis rate. At this level of degradation there is no sign of cell compression ($\times 136$).



Figure 25 Severe degradation of microporous layer in poromeric degraded to 25% of its original tensile energy, after reconditioning the sample was flexed 20 000 times.

The outer skin has remained intact probably due to the lower local hydrolysis rate caused by skin thickness plus mechanical factors. Compression of the cells and polymer flow can be clearly seen in this and the next photograph ($\times 70$).

degradation treatment to 25% of its original tensile energy to break, the SEM photograph in fig. 25 showing that the microporous layer has tended to crumble internally, although the surface skin has remained almost intact. The microporous layer region is shown in fig. 26, and some of the cells around the crack appear to have been compressed by the post-degradation flexing action. The severe degradation treatment given to this particular sample has removed the elasticity and flexibility of the polyurethane foam thus promoting flow and compression. It is unlikely that normal shoes in wear would reach this stage of degradation although some evidence of cell wall fusion can be seen in fig. 22. The reason for the surface skin remaining intact is probably due to the difference in polymer thickness and the resulting influence upon the diffusion of moisture into the polymer. The outermost surface skin is about 100 to 200 times thicker than the cell walls, so that water penetration to the centre of the polymer film would take much longer. The surface skin would thus retain its inherent strength properties much longer than the polymer in the cell walls; also the added strength provided by its much greater thickness is clearly of significance.

Although the SEM has been of particular value in examining this type of degraded material, it has not been possible to detect any changes in the polymer surface as a result of degradation. Further examination of degraded foams without metallisation may provide such information, but the insulating nature of the material may cause difficulties with charging effects.*

Some porometrics resist hydrolysis better, as may be seen from fig. 27 which shows a single crack in the microporous layer. This poromeric had undergone the same hydrolysis and flexing treatment as that shown in fig. 26, but did not show the same degree of cracking: in the enlargement of the crack in fig. 28, no cell wall fusion can be seen. Samples not subjected to hydrolysis, but flexed for the same number of cycles, did not show any cracking.

5. Conclusion

Present footwear upper materials range from the natural fibrous products to a viscoelastic polyurethane foam material. Between these two

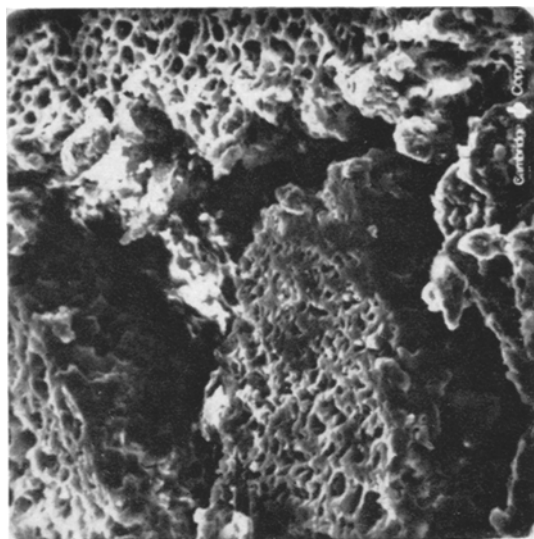


Figure 26 Close-up of microporous layer shown in fig. 25 showing some flow of the polymer and compression of cells ($\times 350$).

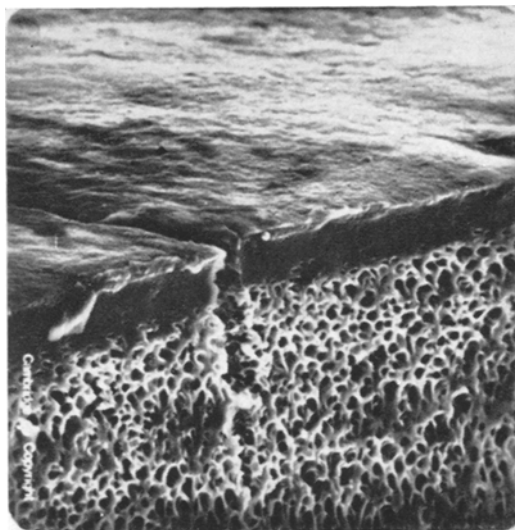


Figure 27 Poromeric degraded in steam at 120°C to 25% of its original tensile energy, followed by 25000 flexes after reconditioning ($\times 357$).

extremes are a large number of other artificial leather compositions. As in other material studies, the scanning electron microscope provides a means of studying the structures and

*Recent experiments with ionic surface active agents e.g. CATALCON K5, have shown that impregnation of the specimen with 5% Aqueous CATALCON K5 effectively prevents charging phenomena and thus metallisation can be omitted. (CATALCON K5 is supplied by J. C. Thompson & Co (Duron) Ltd. Duron Works, Bradford.)

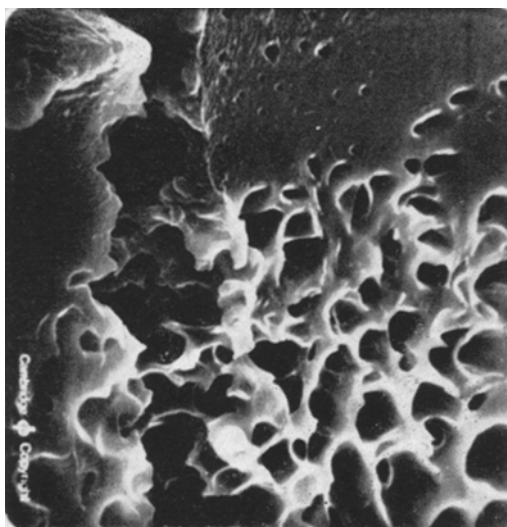


Figure 28 Close-up of crack shown in fig. 27 ($\times 1410$).

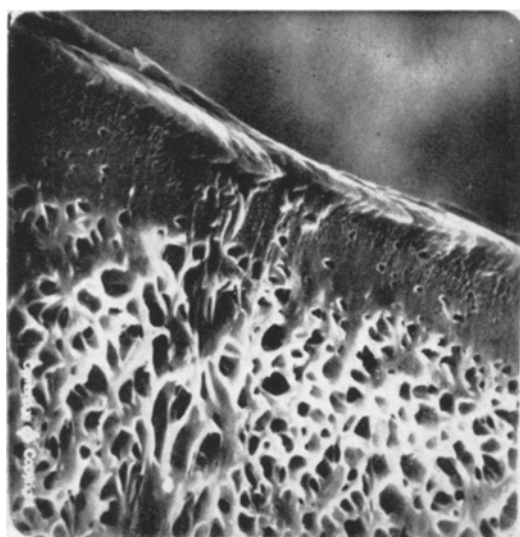


Figure 29 Cross-section of microporous layer of poromeric showing damage due to metallisation ($\times 665$).

fault development in natural and artificial leatherlike materials with directness and detail. The mechanical and chemical stability of these materials has been studied and one important observation has been that cracks resulting from chemical or mechanical degradation tend to occur within the foam structure and propagate to the surface, hence surface examination in service is not enough to determine the degree of degradation. Reasonably good correlation has been found between laboratory testing and the

durability of the materials in wear; this has been confirmed by the SEM photographs.

Great care must be taken with the surface metal coating when preparing foam materials containing viscoelastic polymers for SEM investigations. In some photographs evidence of cell fusion can be seen, a particularly bad example being shown in fig. 29 where either the heat during the metal deposition or spluttering of the heated metal has caused fusion of the surface and distortion of the cell structure. Such faults can be serious, since structural changes in heat sensitive materials such as viscoelastic polymers, can be ambiguous and confuse the interpretation of real structural changes.

Despite these slight problems, there are many applications in the leather and footwear industries in which the SEM can be utilised, such as static and dynamic tensile deformation of poromerics, microbiological attack on materials, failure of metal components, crystallinity of adhesives, failure at bonded junctions, effects of heat setting and embossing, etc. Flexible composite materials such as artificial leathers have received little attention from materials scientists, whose attention has tended to be directed at rigid composites. Flexible materials will no doubt receive more attention in the future and the SEM will be an important tool in their study.

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