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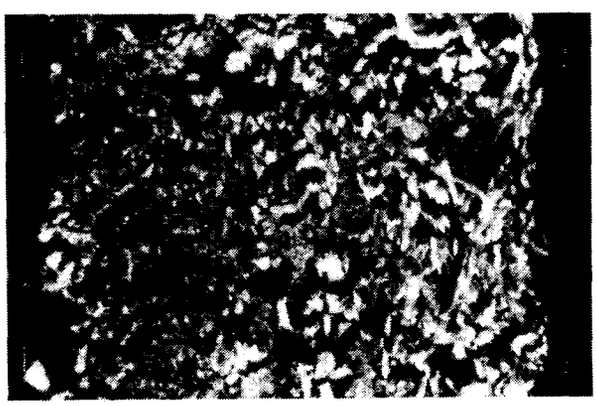
(54) **Process for producing artificial leather similar to real leather by chemically processing synthetic sheet materials.**

(57) Process particularly suitable for sheet material of the type comprising a porous polyurethane resin matrix, the latter containing polyester or polyethylene fibres, and a pressed polyurethane resin cover film patterned to imitate real leather; the said process consisting in treating the said material, inside rotary tanning drums, with a trivalent metal salt solution which is brought up to precipitation pH level in such a manner as to fill the pores in the said polyurethane matrix on the said sheet material with a corresponding hydroxide, after which, the material is treated with a dialdehyde, fireproofing, colouring and softening substances.



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PROCESS FOR PRODUCING ARTIFICIAL LEATHER SIMILAR TO REAL LEATHER BY CHEMICALLY PROCESSING SYNTHETIC SHEET MATERIAL

The present invention relates to a process for producing artificial leather, which looks and feels exactly the same as real tanned leather, using as raw material one of the many synthetic sheet materials known and marketed under various trade names and commonly referred to as "imitation leather". In particular, the present invention relates to a chemical process particularly suitable for synthetic sheet material comprising a porous polyurethane resin matrix, the latter embedded with polyester or polyethylene strengthening fibres, and a compact, pressed polyurethane resin cover film patterned to imitate real leather.

Various synthetic sheet materials are known, made from polymer resins and designed to imitate and replace various types of real leather for a wide range of applications, e.g. for upholstery, shoes, clothing and similar. The said synthetic sheet materials are usually made using

two layers of polyurethane resin placed one on top of the other, the bottom one of which is foamed so as to produce a porous matrix (open- or closed-cell, depending on the type of manufacturing process employed) designed to afford consistency and thickness to the said sheet material, whereas the top layer is compact, usually coated on and pressed with a pattern imitating real leather. Of known materials, the best, and the one most closely resembling real leather in terms of consistency and appearance, is a material of the aforementioned type, i.e. formed of polyurethane resin layers and comprising a porous, open-cell matrix embedded with polyester or polyethylene fibres allowed to move essentially freely along their axes inside the said matrix. A section of such a material is shown in the microphoto in Fig.1, the said material being made and marketed by the Japanese firm "KURARAY CO. Ltd", 1-12-39 Umeda, Kita-ku, OSHAKA 530 (Japan).

A major drawback of known materials of the aforementioned type is that they are highly inflammable and therefore require the addition of fireproofing substances. In addition to being impaired drastically in appearance, to such an extent as to be rendered unusable for a wide range of applications, the look, feel and consistency of the said materials is highly unsatisfactory and still far from competing with the appearance and consistency of real leather.

The aim of the present invention is to provide a chemical process for treating the aforementioned type of synthetic sheet materials in such a manner as to render the appearance and consistency of the same identical to those of real leather, and also for enabling fireproofing of the same.

With this aim in view, the present invention relates to a process for producing artificial leather similar to real leather by chemically processing porous, synthetic sheet material, particularly of the type comprising a porous polyurethane matrix, the latter being embedded with polyester and/or polyethylene fibres, and a pressed polyurethane resin cover film patterned to imitate real leather, characterised by the fact that the said process comprises stages whereby :

. the said synthetic sheet material is treated with a solution of water and bi- and/or trivalent metal salt in such a manner as to cause the said salt solution to permeate essentially the entire section of the said sheet material;

. the said sheet material is then subjected to a greasing process consisting in treating the said material with an emulsion of mineral oil and/or fatty acid esters.

In short, the present Applicant has discovered that, by subjecting porous, synthetic sheet material, imitating real leather, to a process closely resembling tanning, i.e. the process used for preventing real leather from rotting, the appearance and consistency of the said synthetic material were transformed to such an extent as to closely resemble real leather after tanning. The surprising part about this discovery is that tanning is known to have essentially no effect on the appearance and consistency of real leather, the purpose of the process being simply to attack and chemically transform the fibres of which the leather is formed, in such a manner as to prevent the latter from rotting, but without altering the

structure on which the well-known properties of real leather depend. The synthetic sheet materials known as "imitation leather", on the other hand, consist of synthetic fibres which, in addition to being non-perishable in themselves, present polymer chains having essentially saturated links and which are therefore unaffected by commonly-used tanning chemicals. Clearly, therefore, applying the said processes to the said synthetic sheet materials would be considered, not only pointless, but indeed absurd by an average tanner or organic chemist. Experiments conducted by the present Applicant, however, have shown that, by treating porous synthetic sheet material (i.e. having micropores visible only under an electronic microscope) firstly using "pseudo-tanning" salt solutions, i.e. of the type normally employed in known tanning processes or having similar chemical-physical properties, and then subjecting the material so processed to a subsequent greasing process, also of the type to which real leather is subjected and consisting in treating the material with oil emulsions, the said materials absorb and retain internally, in essentially stable manner, at least part of the tanning salt contained in the said salt solutions, in such a manner as to be changed drastically in appearance and consistency after processing; to be more precise, in such a manner as to acquire added consistency and the appearance and feel typical of real tanned leather. It has also been shown that, following such processing, the said materials are less inflammable and may be subjected to any known type of specific dying process for the polymers of which the said sheet material so processed

is formed, thus enabling, if conducted correctly, the production of a finished product extremely similar to real leather and of good appearance. The present Applicant has also surprisingly discovered that the flexibility of the said materials may be improved to such an extent as to be essentially equal to or only slightly inferior to that of real leather by treating the said materials, not only with the said pseudo-tanning salt solution and the said greasing oil, but also with a solution of water and at least one di- or polyaldehyde. Finally, the present Applicant has also surprisingly discovered that, for obtaining the best results, the pseudo-tanning salt solution process must be conducted differently from the real leather tanning process, that is, by appropriately adjusting the pH level of the salt solution by adding a strong base, such as NaOH (sodium hydroxide) in place of the weak bases, such as sodium bicarbonate, usually employed in chromium tanning processes; the processing salts used being preferably trivalent metal sulphates and/or chlorides and/or bi-trivalent metal sulphates (i.e. metals, such as iron, capable of assuming various grades of oxidation).

According to the present invention, the porous, synthetic sheet material, usually in strips of about 10 m in length, is collected and tied firmly into bales of such a size as to enable it to be loaded inside a rotary drum, e.g. of the type normally employed for tanning real leather. The bales of synthetic sheet material so formed are than placed inside the said drums which are than started up and the material chemically processed by feeding the vari

ous chemical solutions into the drum as it is turned. In more detail, according to the present invention, the porous synthetic sheet material is first subjected to a "soaking" process essentially consisting in treating the material for ten minutes to an hour at 50-60°C in a solution of water and surface-active substances. Upon completion of the said "soaking" stage, which provides for soaking the material thoroughly and filling practically all the pores in the same with liquid, the rotary drum is filled with the first processing solution consisting in the said bi- and/or trivalent metal salt solution. The synthetic sheet material is treated in the said salt solution for about ten minutes to an hour, until the said solution permeates essentially the entire section of the material, after which, it is treated with a pseudo-tanning caustic soda solution for bringing the pH level up to about 7. At this point, the solution is brought up to a temperature of about 60°C and the pH level raised further, though never over 7.5, by precipitating part of the salt contained in the solution in the form of hydroxides, which precipitate in the solution essentially in the form of a gel. As prolonged treatment of the sheet material in the said pseudo-tanning salt solution causes part of the pores on the said material to be fully saturated, during the precipitation stage, part of the hydroxides precipitate in gel form straight into the said pores which are thus filled with gel to produce a fairly noticeable increase in the weight and consistency of the sheet material so processed. Furthermore, as hydroxides are known to be fairly good fireproofing substances, the synthetic sheet material so

processed is considerably less inflammable than in its original form. Upon completion of the precipitation stage, the sheet material is washed to remove any surface traces of hydroxide, after which, the material is treated for ten minutes to an hour, still inside the said rotary drum, with a solution of water and 5-10% by weight of a di- or polyaldehyde. Dialdehyde processing of the material has been found to afford flexibility, as well as maintaining the superior properties acquired by the material in normal use. Finally, the material so processed is put through a number of further processes, the most important of which - greasing - has been found to be essential for obtaining the required results, i.e. for transforming the original synthetic material into one identical to real leather. The said greasing process, conducted inside rotary drums, is identical to the real leather greasing process, except that use may be made in differently of mineral oils or, preferably, higher fatty acid ester emulsion, preferably charged with sulphur, at a temperature of about 60°C for a few minutes to an hour. When treating composite material, i.e. having synthetic fibres embedded in the porous synthetic matrix, the said greasing process is particularly effective in that the esters and oils, which would not normally be retained by compact synthetic resins, are retained by the synthetic fibres and pores in the processed material in such a manner as to give the latter the characteristic appearance of real leather. Furthermore, the said oils and esters also improve fibre flow inside the porous matrix in such a manner as to give the processed material the character-

istic consistency and feel of real leather. Further processes the material may be subjected to according to the process covered by the present invention include dying, which is conducted in known manner, i.e. after washing the material in cold water; and fireproofing which, according to the present invention, is performed by treating the material, in a rotary drum for a few minutes to an hour, in a fireproofing solution containing, in place of the normal fireproofing substances employed (with little success) in known fireproofing processes, retarding substances of the type employed for extinguishing forest fires, the said substances being marketed under various trade names and also containing ammonium salts. Though the said retarding substances are absorbed by the said sheet material in such a manner as to render the latter essentially inflammable, the resulting material is made so stiff as to be totally unusable. Such stiffening, however, is overcome according to the present invention by combining the fireproofing/retarding solution treatment with a finish process whereby the sheet material is treated, again in a rotary drum, in a solution containing ordinary commercial softening substances, e.g. based on lauric acid salts. In more detail, according to the present invention, the said synthetic sheet material is treated in a fireproofing solution of PIROFLAM (registered trade mark) and then in a softening solution of TRIANOL SP (registered trade mark) to which is added, according to the present invention, a small percentage of PIROFLAM to prevent the ammonium and retarding salts absorbed by the material in the previous fireproofing process from being dissolved. Final

ly, the material is dried in hot air, after which, the bales are undone and the sheet material rolled up and sent off for finishing in exactly the same way as for real leather. As the said finishing process is conducted in known manner and does not come within the scope of the present invention, no mention will be made of it herein. The present Applicant has discovered that the process according to the present invention enables the production of really good-quality artificial leather, practically identical to real leather, only when applied to a particular group of synthetic sheet materials or "imitation leather" comprising a porous polyurethane resin matrix, the latter embedded with polyester or polyethylene fibres, and a compact, pressed polyurethane resin cover film. In this case, according to the present invention, the dying stage, after greasing the material with esters charged with sulphur, is performed by treating the sheet material inside a rotary drum for at least two hours in a mixture of complex metal colouring substances specially devised for polyester or polyurethane polymer fibres, the said process being conducted in such a manner that the colouring substances adhere successively to the said sheet material. The process is conducted for about at least an hour at approximately 40°C, after which, the temperature is raised to about 60°C for the remainder of the dying stage. The material is then dried by means of forced hot-air ventilation at about 70°C inside the drum, preferably turning at a speed of 4-6 rpm. The sheet material employed is preferably 0.3 to 2 mm thick, depending on what it is to be used for, and, after processing according to the

present invention, looks essentially as shown in the microphoto in Fig.2. The two microphotos in Fig.s 1 and 2 clearly show the difference in structure and appearance, even at microscope level, between the said material before (Fig.1) and after (Fig.2) processing according to the present invention. The latter therefore clearly provides for transforming relatively poor-quality "imitation leather" into very good-quality artificial leather with which to manufacture upholstery, shoes, clothing and similar of essentially the same appearance and quality as those made using real leather.

The present invention will now be described by way of a number of non-limiting examples.

EXAMPLE I

Twelve 10 m long strips of porous, synthetic sheet material, as shown in the microphoto in Fig.1, were folded and tied up into twelve 250 x 120 x 120 cm bales and loaded inside a rotary drum of about 5.6 cu.m in volume. The material employed was composed of a layer of porous polyurethane resin covered with a layer of compact polyurethane resin pressed to imitate calf leather; the porous polyurethane layer containing a high number of polyester fibres oriented in various directions and housed in sliding manner inside the polyurethane matrix. The material was 1.2 mm thick and is produced and marketed by KURARAY CO. Ltd, 1-12-39, Umeda, Kita-ku, OSHAKA 530 (Japan).

After loading the said material inside the drum, the latter was filled with 650 litres of water containing surface-active substances and the solution brought up to 60°C. After running the drum at a speed of 15 rpm for 20

minutes, the water and surface-active substance solution was drained off and the drum filled with 650 litres of solution containing 30% by weight of ferric sulphate, which was brought up to a pH level of 3.2 and a temperature of 60°C. After running the drum for about 40 minutes, the pH level was raised to 7.1, by adding NaOH 10 N, and the temperature to 60°C, in such a manner as to precipitate $Fe(OH)_3$ with abundant flocculation. Finally, after rinsing thoroughly in water and draining off the used-up solution, the drum, still turning, was filled with 650 litres of a solution of water and 6% by weight of aspartic aldehyde. After running the drum for 42 minutes, the said solution was drained off and the sheet material treated, with the drum still turning, for 45 minutes at 60°C in 650 litres of solution containing 30% by weight of sulphur-charged fatty acid esters having roughly 17 to 22 carbon atoms. Following such processing, the sheet material was dyed, still inside the turning drum, by treating it with a solution of water and 3% of BASACRIL (registered trade mark) for 55 minutes at 40°C, then for an hour at 60°C, after which, it was rinsed thoroughly. Finally, the material was treated, still inside the turning drum, with 252.5 litres of a solution of water and 60% by weight of PIROFLAM (registered trade mark) for 30 minutes, then with 56.25 litres of a solution of water and 30% by weight of PIROFLAM and 20% by weight of TRIANOL SP (registered trade mark) for 15 minutes. The material was then dried with hot air at 60°C inside the drum turning at a speed of 6 rpm.

EXAMPLE II

Twelve 10 mm strips of synthetic material as in Example I were treated in exactly the same way as in Example I, but using chromium sulphate in place of ferric sulphate. The resulting material presented an excellent consistency and feel and a satisfactory outward appearance as in Example I.

EXAMPLE III

The materials used in Examples I and II were treated in the same way as in Example I, but using a salt solution of ferrous instead of ferric sulphate. The resulting material after processing was identical to that of Example I.

EXAMPLE IV

The material used in Example I was treated in exactly the same way as in Example I, but using glutaric instead of aspartic aldehyde. The resulting material presented a high degree of flexibility as well as a fairly good appearance.

EXAMPLE V

After processing, the sheet material used in Example I was formed into twenty 20 x 20 cm test pieces and comparison-tested, together with corresponding test pieces of tanned calf leather of the same size, as to tensile, abrasion and bending resistance. The results are shown in Table I.

TABLE I

	Real calf leather	Polyurethane-matrix resin + polyester fibres after processing
Tensile resistance	G	E

Abrasion resistance	G	G
Bending resistance	G	G

(E = Excellent; G = Good; P = Poor)

EXAMPLE VI

The sheet material used in Example I was formed, before and after processing, into 20 x 20 cm test pieces which were then combustion-tested as per Standard Federation standards n°302 (horizontal test piece). Four test pieces of processed material dyed different colours were comparison-tested with four pieces of unprocessed raw material. The results expressed in terms of combustion rate (mm/min) are shown in Table II.

TABLE II

Test piece	Unprocessed material	Processed material
Yellow	181.5 mm/min	zero
Brown	181 mm/min	zero
Black	180 mm/min	zero
Khaki	182 mm/min	zero

EXAMPLE VII

The process described in Example I was applied to a starting sheet material consisting of a 0.8 mm thick, two-ply sheet of polyurethane foam covered with a compact polyurethane film, of the type normally used for upholstering vehicle sunshields. The resulting product, as described in Examples V and VI, gave the same results as those shown in Tables I and II, though of inferior quality as compared with the finished product in Example I.

CLAIMS

1) - Process for producing artificial leather similar to real leather by chemically processing porous, synthetic sheet material, particularly of the type comprising a porous polyurethane matrix, the latter being embedded with polyester and/or polyethylene fibres, and a pressed polyurethane resin cover film patterned to imitate real leather, characterised by the fact that the said process comprises stages whereby :

. the said synthetic sheet material is treated with a solution of water and bi- and/or trivalent metal salt in such a manner as to cause the said salt solution to permeate essentially the entire section of the said sheet material;

. the said sheet material is then subjected to a greasing process consisting in treating the said material with an emulsion of mineral oil and/or fatty acid esters.

2) - Process according to Claim 1, characterised by the fact that, straight after being treated in the said salt solution, the said sheet material is treated in a solution of water and a di- or polyaldehyde.

3) - Process according to Claim 1 or 2, characterised by the fact that, upon completion of the said salt solution treatment, the said salt solution is brought to such a chemical-physical condition as to precipitate, directly inside the pores of the said sheet material, the corresponding hydroxide in the said bi- and/or trivalent metal salt in the form of a gel.

4) - Process according to Claim 3, characterised by the

fact that the said salt solution is caused to precipitate by raising its pH value by adding a strong base.

5) - Process according to one of the foregoing Claims, characterised by the fact that the said metal salt is a sulphate.

6) - Process according to one of the foregoing Claims, characterised by the fact that a synthetic sheet material about 0.3 to 2 mm in thickness is employed, the said material being collected and tied into suitably-sized bales which may be placed inside a rotary drum of the type employed for tanning real leather.

7) - Process according to Claim 1, characterised by the fact that the said synthetic sheet material is first placed inside a rotary tanning-type drum, after which, it is treated in water containing surface-active substances, after which, it is treated in a trivalent metal sulphate salt solution, at first maintaining the pH value of the said solution around 3.2 and then charging the tanning solution with NaOH so as to raise the pH value to about 7-7.5 and so precipitate the corresponding hydroxide, after which, the said material is washed and treated in a 5-10% dialdehyde solution.

8) - Process according to Claim 7, characterised by the fact that, after dialdehyde treatment, the said synthetic sheet material is greased in a solution containing 30% by weight of sulphur-charged oil, dyed using appropriate colouring agents, washed, treated in a fireproofing solution and, finally, treated in a softening solution charged with the said fireproofing solution.

9) - Process according to Claim 8, characterised by the

fact that the said synthetic sheet material consists of a composite material comprising polyester and/or polyethylene fibres embedded in a porous polyurethane foam matrix, and is dyed in a rotary drum using a 3% solution of a mixture of at least one complex metal colouring agent, specifically for polyester fibres, and at least one complex metal colouring agent specifically for polyurethane resins, the said colouring solution being initially maintained at a temperature of about 40°C and then raised to about 60°C after about at least one hour's treatment.

10) - Process according to one of the foregoing Claims, characterised by the fact that the said synthetic sheet material is finally dried in hot air and rolled up.

11) - Process for producing artificial leather similar to real leather by chemically processing porous synthetic sheet material as described and claimed in the foregoing Claims.

12) - Artificial leather for manufacturing upholstery, shoes, clothing and similar, characterised by the fact that it is produced using the process according to one of Claims 1 to 10.

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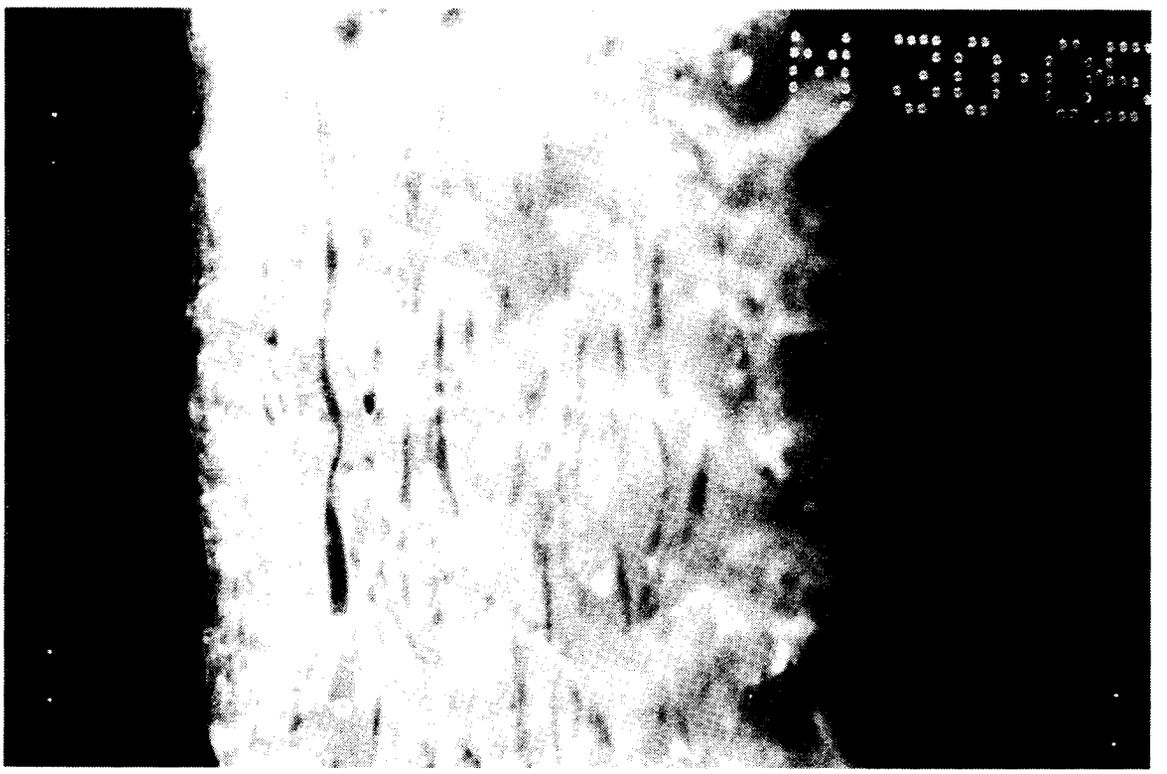

Fig.1

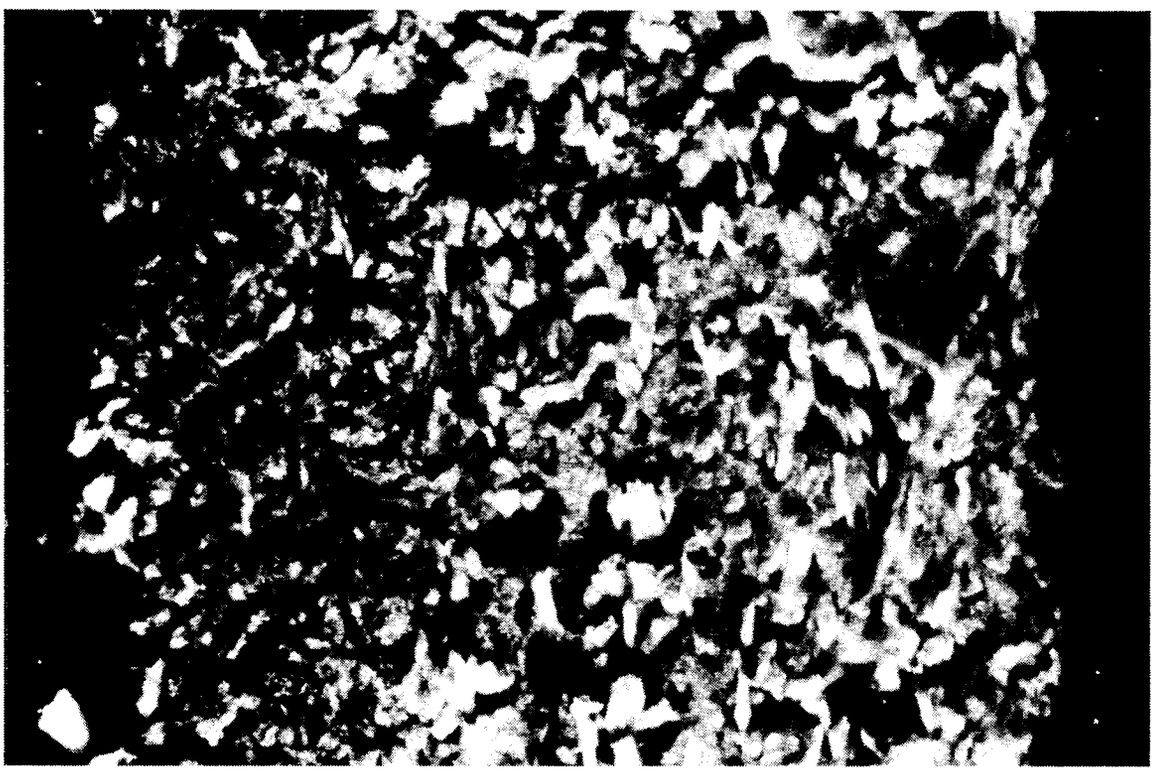

Fig.2