

# Latest Progress of Man-Made Leather

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## 1. Introduction

Historically, a production of artificial leather began with a combination of woven cloth and coating resin. The development of artificial leather was closely followed to the development of synthetic resins. The significant development for the artificial leather was resulted from the development of polyurethane resin following PVC resin and polyamides. However, recently, owing to advances in processing techniques for the resin and fiber, the improvement in performance of the artificial leather has been remarkable. Thanks in particular to the development of a vapor permeable porous sheet through coagulation using a wet process and to the development of a special fiber consisting of microfibers through an extraction method, we have arrived at the artificial leather with characteristics similar to a natural leather for use in the shoe upper and clothing field.

This lecture will cover about the development of the manufacturing techniques for the substrate of man-made leather by reviewing the important techniques shown in the patents. And I will explain the recent tendency of the man-made leather made of special fibers.

## 2. Development of Artificial Leather

Attempts to make leather synthetics were made fairly long ago and the patent of Lewis Cornides in England in 1885 can be given as one example. By coating pyroxyline paints on

cloth, he obtained a pyroxyline leather<sup>1</sup>. This pyroxyline leather was used for almost half a century until the arrival of PVC leather.

The PVC leather obtained by coating PVC resin on cloth was first produced around in 1930 in the U. S. A. and Germany and then in Japan about in 1950. Thereafter, the main movement of PVC leather changed from plane sheet to foam sheet from around 1960. Today it is mainly used for upholstery products because of advantages in the price and processing of PVC resin<sup>2</sup>. It maintains a stable position among artificial leathers. However, the real progress had not been made into the high quality and valuable products represented by shoe uppers up to date.

On the other hand, nylon coated fabric, commonly called NCF, started with the development of formation techniques for a nylon membrane by a wet method by Du Pont in 1944<sup>3</sup>. NCF has a good appearance and touch as well as vapor permeability that is more similar to natural leather than PVC leather and gained a good reputation as a natural leather substitute in Japan<sup>4</sup>. However, it was also not used for shoe uppers because of problems with flexing fatigue resistance but was very popular in the sack and bag fields. And because of the spread of polyurethane resin after that, its mass production has decreased in recent years.

Du Pont did not commercially produce NCF but worked on development of an artificial leather more like natural leather and developed Corfam in 1963<sup>5</sup>. This Corfam is made up of

three layers; a microporous polyurethane surface layer, a mid woven cloth layer and a substrate layer consisting of non-woven cloth and polyurethane<sup>6</sup>. Appearance, hand, vapour permeability and other characteristics are similar to natural leather and it was in the limelight as an artificial leather since it could be used as an ordinary shoe upper. At that time, it did not remain with Du Pont, but the development of artificial leather that could be used as uppers because of its durability and performance, spread to all countries of the world.

The development of the artificial leather was very fast in particular in Japan which depends on imports of 90% of raw hides with wide fluctuation in quantity and price. In 1964 to 1966, soon, after Corfam was announced, four companies in Japan entered into commercial production.

In addition, the information on the development and commercial production of the artificial leather was continuously brought from the U. S. A. and West Germany. Then, this series of newly developed artificial leathers was distinguished from other artificial leathers because of its durability and performance, so it could be used for shoe uppers.

### **3. Grain Type of Man-Made Leather**

#### **3-1. Changes in the Man-Made Leather Field**

After the arrival of Corfam, man-made leathers have appeared one after the other on the artificial leather market and in the '60s manufacturers who took up commercial production of man-made leather exceeded 10 in various countries around the world. However, these man-made leathers did not necessarily follow an orderly development.

These man-made leathers not only had the performance for use as shoe upper, uniform

quality of synthetics and easy care but also were severely judged from the point of view of the efficiency in shoe making and wear ability as shoes. First in 1971 Du Pont stopped the production of Corfam and then took all three layered materials of the Corfam type off the market. In the beginning of the '70s, as the tendency toward softness in material grew on the natural leather market, the demand for soft man-made leather increased. For that reason Glanzstoff of West Germany stopped the production of Xylee in 1976. It was a two-layered material but belonged to the hard type so they took it off the market.

The soft type of man-made leather consisting of a single polyurethane layer or special fibers and polyurethane, has built up a wide market due to the good efficiency in shoe making<sup>7</sup>. With this progress, man-made leather was polarized into two tendencies, one for the good efficiency in shoe making and the other toward the natural leather. But recently the demand for man-made leather that is similar to natural leather is growing in the shoe field in order to make the high quality and valuable products. With this as a background, each company is working on the development of new products, and Clarino which went into full-scale production last year is one material that can meet the demands of users. Leather research associations in England, West Germany etc. have evaluated it very highly<sup>8</sup>.

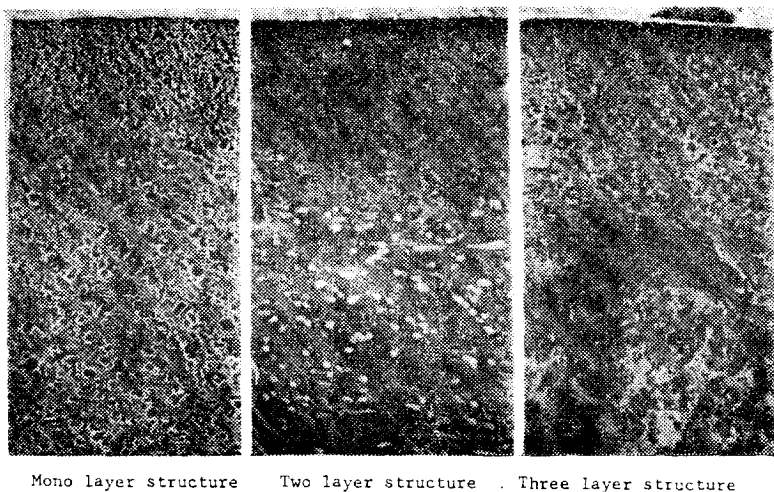
#### **3-2. Progress in Production Techniques**

The texture and structure of natural leather are made up of two layers. The upper grain layer is comparatively hard and shows good wear resistance. The lower reticulum is thicker than the upper layer and has some excellent features such as toughness, elasticity, vapor permeability and water permeability. Each of

these layers is composed of a combination of fiber protein and collagen which is made of keratin elastin<sup>9</sup>. Man-made leather uses a polyurethane porous layer as a substitute for the part which corresponds to the surface layer of the natural leather that microfibers are closely interlacing. The substrate made from a needle punched non-woven cloth and a binder elastic resin is used as a substitute of the lower reticulum of the natural leather. However in order to make up for the low initial modulus caused by lack in the degree of mechanical interlacing of fiber and of the heat contracting

treatment to improve needle punching of the non-woven cloth is often introduced into the substrate.

From these reasons, Corfam and most early man-made leathers had a 3-layered structure. Among these, Clarino with its two layered structure using non-woven consisting of special fibers and Porvair with its one layered structure using all porous polyurethane were different. We can distinguish between three types of man-made leather appeared on the market but they were all the same in that the outer layer was porous polyurethane.



**Figure 1.** Gross sections of three types of man-made leathers.

Consequently, the series of man-made leathers shown in Fig. 1 were also called Poromeric. Thereafter, synthetics were looked for in order that all the characteristics of man-made leather could be made to approximate all the characteristics of natural leather. Attempts to produce the man-made leather imitating the collagen fiber structure of natural leather began by combining polyolefin microfiber and polyamide binder<sup>10</sup>. The methods for making the substrate from special fiber and elastic resin

and for extracting one element from two component fiber formed non-woven cloth were developed<sup>11</sup>. The man-made leather from polyamide fiber and polyurethane resin was commercially produced.

Then various methods for producing microfibers like collagen were developed and suede products using these special fibers appeared one after the other on the market. In the grain type field, demands for softness increased and man-made leather, Clarino F using special

fibers consisting microfibers as the substrate fibers with outstanding softness, made its appearance<sup>12</sup>.

### 3-3. Technique for Making Substrate

As I said before, there is one substrate consisting of resin and a non-woven interlaced and another substrate with a single porous resin. Nowadays the former substrats is common and I will explain that one.

Fibers used in the substrate can be classified into three types.

- (1) Substrate with a base of non-woven cloth made from short cut fibers having a shorter length than 20mm<sup>13</sup>.
- (2) Substrate with a base of non-woven cloth made from staple fiber of an ordinary length.
- (3) Substrate with a base of filament<sup>14</sup>.

Substrate (2) is the most common for man-made leather but it is not as easy to make as (1) and (3). However, because the needle-punching of the non-woven cloth is easy and its interlacing is superior, it is easy to make a substrate that is soft and has a leather like hand. In addition, various improvements have been made on staple fiber. For example, there are many methods being proposed, a method for improving the interlacing by giving a heat shrinking ability and revealability of crimp and a method for improving the substrate by obtaining special fiber from multi-component fiber<sup>11, 15</sup>.

### 3-4. Technique for Making Surface Layer

Rubber elastic resins like polyurethane are used in the surface layer. There are many patents aiming at improving structural stability for formability of the porous sheet and for heat and solution resistance. And there are also many patents for the special structure of

the porous layer<sup>16, 17, 18, 19</sup>. We can obtain the following conclusion from these important techniques.

In order to make stable porous sheet, basically we must aim at controlling the formation of the skin layer and eliminating the difference between the initial and final solidifying condition as well as try for stable solidification without reorientation of the molecules in the later process. Various additives can be used and the solidifying speed can be control by the solvent composition, the type of the non solvents and the temperature.

## 4. Suede Like Man-Made Leather

### 4-1. Advances in Production, Techniques

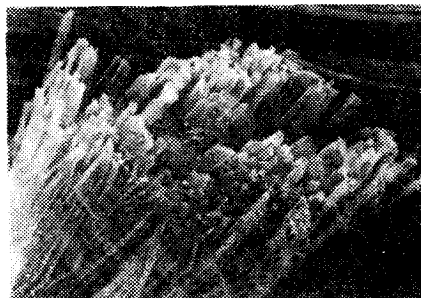
In 1963, Du Pont had developed a fibrous suede using fine fibers. From the patents and products, it was presumed that they made suede like sheet with a fiber nap by buffing with sand paper the surface of the substrate made from shrunk PET non-woven cloth consist of 0.5dr fibers and a polyurethane binder. However, this product was hardly seen on the market because it could not reproduce sufficiently well the special touch and appearance of the suede surface of natural leather<sup>20</sup>.

Thereafter, a technique for producing a substrate from special fiber which was obtained by extracting one element from two components fiber was developed. The special feature of this production technique was the obtaining of a synthetic fiber mat consisting of microfibers that was not possible in usual methods of making card web. Based on this technique, fibrous man-made suede with surface features of leather suede were produced on a trial basis. We have already seen one example in the patent presented in 1964<sup>21</sup>.

If we look at present day fibrous man-made

suede products on the market, we see that the fibers are made by special spinning techniques of various companies. However, the basic process was the same for all companies i. e. after using fiber obtained by spinning more than two types of polymers with different characteristics and making that fiber into sheet, they obtained a sheet surface of microfibrs by an extracting or mechanical method and then obtained nap surface by buffing.

Fig.2 shows one example of a basic fiber. Before treatment with solvent, many dispersion elements in the fiber have hidden by the matrix.



**Figure 2.** Gross section of microfibrs in a special fiber used for clarino F.



Calf suede



Amara

**Figure 3.** Gross sections of suede like leather and calfe suede.

By treating the matrix of this fiber with a solvent the dispersions become microfibrs. As seen in an enlargement of these fibers one microfibr has a diameter of  $0.5\sim 2\mu$ . The structure of fibrous suede products made using this type of special fiber is shown in Fig. 3. This suede like man-made leather is made, modelled after calf suede and its cross section structure is very similar to calf suede<sup>22</sup>.

Recent fibrous suede can be a fashionable material answering demands for diversification in clothing life as an apparel material with many special features. Its market development is expected in the future. Man-made leather manufacturers have to know the user's demands. The important theme will be the direction of man-made leather in the future.

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