Harro Träubel

New Materials Permeable to Water Vapor

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With 106 Figures

Springer

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ISBN 3-540-64946-8 Springer-Verlag Berlin Heidelberg New York

Library of Congress Cataloging-in Publication Data

Träubel, Harro,
New materials permeable to water vapor / Harro Träubel.
p. cm.
Includes bibliographical references and index.
ISBN 3-540-64946-8 (hc.: alk. paper)
1. Porous materials – Permeability. 2. Water vapor transport.
3. Fibrous materials – Permeability. 4. Synthetic products – Permeability. I. Title.
TA418.9.P6T75 1999 620.1'16 – dc21 99-17767 CIP

Cover design: de'blik, Berlin
Production: ProduServ GmbH Verlagsservice, Berlin
Typesetting: Fotosatz-Service Köhler GmbH, Würzburg

SPIN: 10634869 02/3020 - 5 4 3 2 1 0 - Printed on acid-free paper

New Materials Permeable to Water Vapor

Springer
Berlin
Heidelberg
New York
Barcelona
Hong Kong
London
Milan
Paris
Singapur
Tokyo

Preface

During the past 40 years many patents and articles have been published which describe methods and materials for water vapor permeable materials. These materials were primarily designed to substitute leather in its look and performance. Later other industrial applications were found where microporosity or water vapor permeability could be used.

The aim of this book is to give a survey of this matter, describing in an abridged way all the publications existing up to 1996.

The terms "water vapor permeable material", "artificial leather", "synthetic leather", "leather substitute" or "man-made leather" are defined, and the special characteristics of leather are compared with its substitutes.

Then the special methods used to produce microporous and hydrophilic materials, suitable substrates, end uses in fields other than wearing purposes, testing methods, as well as patent strategies and ecological behavior are discussed.

Each chapter starts with general remarks about the the specific characteristics of its motto; then published examples belonging to the subjects of the chapter are described.

Sources of most of the literature have been the "Textilbericht" and the "Hochmolekularbericht" of Bayer AG – today no longer in existence. Additionally, Chemical Abstracts and original publications in the form of patents and articles in books and journals are used. During the past 40 years many patents and articles have been published which describe methods and materials for water vapor permeable materials. These materials were primarily designed to substitute leather in its look and performance.

One positive point of this book seems to be the literature published before 1980, because in commercial electronic data systems these publications have mostly up to now not been available.

I would like to express my thanks to the following people. W. Held, Dr. J. Pedain, Dr. M. Rolf and Dr. P Suchanek for granting me the permission to have this work published and to Dr. Holm and D. I. Reinfand for preparing the microphotos – even if it was more than 20 years ago. My thanks are also expressed to Dr. B. Zorn who helped to write the first draft and assisted in the organization of the material in a logical form.

My special thanks are expressed to Mrs. Käfinger for her patience in her attempts to improve my English and to eliminate my German language-based expressions.

May 1999 Harro Träubel

Abbrevations

ABR	acrylonitrile-styrene polymer
BOD	Biological oxygen demand (Degradable organic substances by the action of micro organisms e. g. after a period of 5 d = BOD_5)
cip	Continuation in part (If the claims of a patent are not granted in their original manner, the patent may be reissued in parts)
CMC	Carboxymethyl cellulose
COD	Chemical oxygen demand (Consumption of organic material by oxidation with potassium dichromate)
DABCO	Diazabicyclooctane (A catalyst for isocyanate-hydroxyl reactions)
div.	Division (If the claims in a patent are to broad, do not correspond to the examples or are not homogeneous, parts of the patent can be separated and newly issued. This new issue is named patent application no. xx division of patent application yy which can be abandoned or reissued with claims being smaller than in the original application.)
DMAc	Dimethylacetamide (Solvent)
DMF	Dimethylformamide (Solvent)
DMSO	Dimethyl sulfoxide (Solvent)
FC	Fluorocarbon (Water- and stain-resistant agents)
H12MDA	4,4′-Diaminodicyclohexylmethane
H12MDA	4,4′-Diaminodicyclohexylmethane (MDA perhydrated)
H12MDI	4,4′-Diiisocyanatodicyclohexylmethane
H12MDI	Dicyclohexylmethane-4,4′-diisocyanate (MDI perhydrated)
HDA	Hexamethylenediamine
HDI	Hexamethylenediisocyanate
HDPE	High density polyethylene
HF	High frequency
IPDA	Isophoron diamine
IPDI	Isophoron diisocyanate
LDPE	Low density polyethylene
MDA	4,4′-Diaminodiphenylmethane
MDI	4,4′-Diisocyanatodiphenylmethane
MEK	Methyl ethyl ketone (Solvent)
MSA	Maleic acid–styrene polymer
PE	Polyether
PES	Polyester

PTFE	Polytetrafluoroethylene
PUR	Polyurethane
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
SBR	Styrene-butadiene polymer
SEM	Scanning electronic micrograph
TDA	Toluenediamine
TDI	Toluene diisocyanate
THF	Tetrahydrofurane (Solvent)
WDD	Wasserdampfdurchlässigkeit (Water vapor permeability)

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Part 1

Leather and Artificial Leather

After launching a synthetic substitute for silk and other natural products in the 1930s, chemists also wanted to develop a synthetic material able to substitute leather. This was a difficult task, but finally in the 1950s the chemical company DuPont developed CORFAM®, a substitute for leather.

CORFAM® was microporous, i.e. water vapor permeable, and was the first material which not only was optically similar to leather, like PVC or nitrocellulose coated textiles, but was also able to transport perspiration from inside to outside as long as a shoe consisted entirely of it.

Due to its special performance, leather and its properties will be discussed in the first chapters.

CHAPTER 1

Leather

Even at rest, humans lose about 30 g of water an hour through their skin. Physical activity and sport can increase this to 1000 g an hour. We often wear garments to protect ourselves against wind, rain, heat and cold. The denser the fabric, the better it protects us against the elements. However, such fabrics tend to be uncomfortable because the water vapor released by the skin as perspiration cannot escape quickly enough. Mountaineers, walkers and skiers know all about this problem. Coats and jackets made of PVC imitation leather provide excellent protection against wind and rain but are virtually synonymous with extremely poor wear comfort.

Textiles that have been given a water-repellent finish lose their water-repellent properties if they are exposed to high mechanical strain and, finally, when they are cleaned. Furthermore, fabrics that are really windproof are generally very heavy.

What options do we have if we wish to combine wear comfort with protection against the elements? The following ensure good wear comfort:

- Water-repellent fabrics
- Animal skins (leather and furs)
- Microporous garments
- Hydrophilic coatings

We can try to imitate nature by protecting ourselves with the skin of an animal or due to the fact that this skin will after a while decompose, with a modified version of an animal skin. In other words, we can wear *fur* or *leather* coats, clothes or jackets. These protect us against wind and rain and, provided the tanner did his job properly, they transport perspiration outward.

The drawback is that leather is often heavier than we would like. Moreover, it is not normally hard-wearing enough to be used in sportswear. Laundering and dry cleaning can be a problem for leather.

The next possibility is: We can give textiles a *microporous* coating, preferably using polymers with good physical properties. Such coatings allow water vapor to pass through but keep out wind and water.

However, there are also problems associated with such coatings: micropores weaken the polymer structure. Consequently, coatings are usually applied to the reverse (i.e. inner) side of fabrics, or the microporous membrane is sandwiched between two layers of textile material, a wind and waterproof outer coating and a lining. This is the only way of guaranteeing that the membrane is not destroyed by abrasion or rubbing during wear (see Chap. 27).

Another possibility is to produce a polymer that has good physical prope and is *hydrophilic*. The hydrophilic properties would ensure that the poly can be applied as a homogenous film. Water vapor could migrate through this homogenous film by means of adsorption and desorption. Such polymers could be applied to a textile substrate as an outer coating and be used to manufacture thin and extremely lightweight garments. Unfortunately, it is not as easy as it sounds.

Hydrophilic polymers take up water, which acts as a plasticizer and weakens the resistance of the film to abrasion and rubbing. Worse, when drops of rain come into contact with the polymer, they cause localized swelling, producing unsightly blisters at the point of contact. These often remain once the rain ha stopped and the water of the blisters has evaporated – a situation which co lead to complaints from consumers.

Due to the fact that leather is a kind of a model for the solutions chemist could offer, the characteristic properties of leather are discussed first.

The starting materials for leather are animal skins and hides. Animal skins a byproducts of slaughter houses producing meat. Statistically 7 % of the weight o cattle consists of the hide. Cattle are only slaughtered for their meat – never for their hides [6].

Leather is regarded as the first material human beings produced by chemical methods. Paintings more than 20,000 years old show the use of leather (Fig. 1-1). Being a by product of meat production, hides and skins have limited availability. Hides and skins are both available in quantities depending on the worldwide demand for meat and they are sold and bought on a worldwide basis.

The price of hides and skins is established at auctions. Due to a worldwide marketing system the price level is also influenced by the exchange rate of the

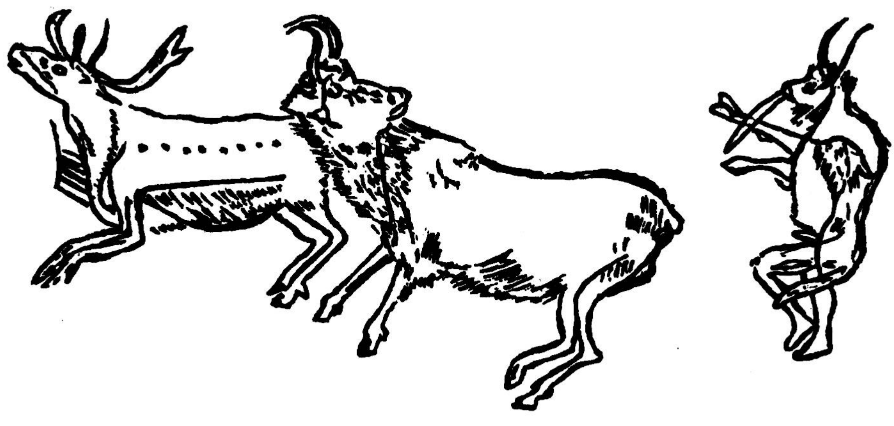

Fig. 1-1. Painting of ice age humans: Stone-Age painting from the caves of Les Trois Frères by Montesquieu-Aventès (Ariège): A magician clothed in an animal skin which has presumably been tanned. The magician is playing a flute and charming animals. He would not have been able to get near these animals while he was wearing an untanned skin smelling of blood or mold. Middle Magdalenian period, approximately 20,000 years old

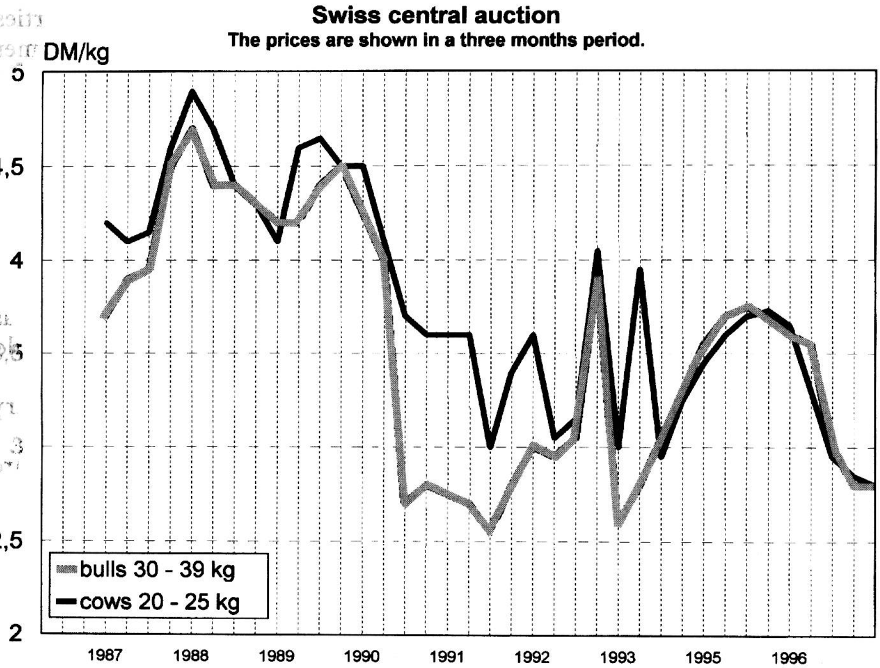

Fig. 1-2. Variation in hide prices (graph courtesy of B. Herrmann)

dollar against local currencies [2]. Their price level has an analogue movement to fluctuations of shares. Figure 1-2 shows the changes in hide prices over a ten-year period in DM.

The availability of leather differs from other natural materials such as wood, wool, natural rubber etc. These materials are not byproducts from other areas. They are produced by middle- or long-term breeding methods. Their quantity and quality is not determined by external factors.

The production, treatment after the killing of the animal and the preservation of the raw hides are decisive for the quality of the leather that can be made out of it.

The raw material for leather is produced in countries with large numbers of cattle. Countries with a large cattle production are USA, Brazil, Argentina, etc. Australia and New Zealand are big producers of sheep skins. China, India and many African countries produce large quantities of goat skins.

The availability of hides does not depend directly on the cattle living in a country. This availability depends on the killing rate of the animals, which depends on the meat production and consumption. Meat consumption is high in countries with a high standard of living like those in the USA and Western Europe. A survey of the production of hides and skins is given in Fig. 1-3.

The hides and skins are transformed into leather – most of the leather being used to produce shoes (Fig. 1-4).

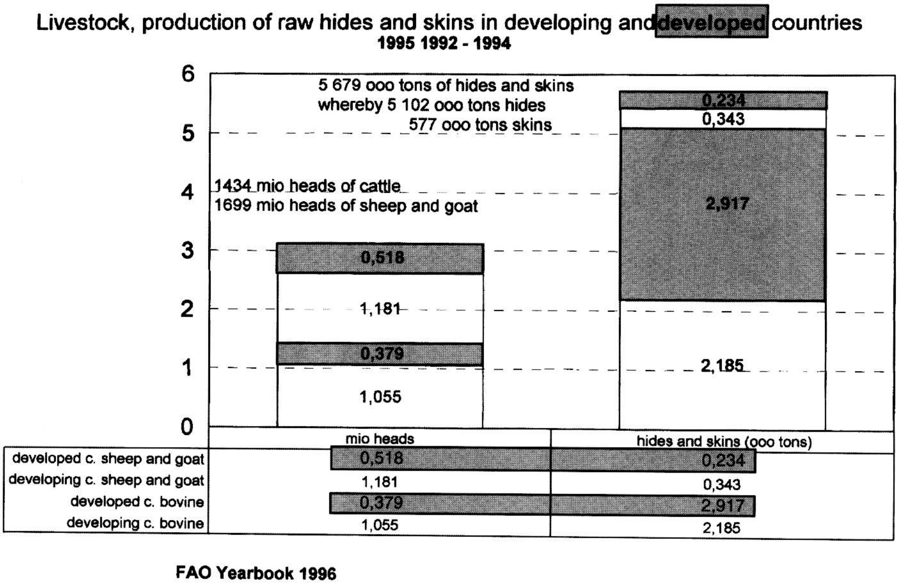

Fig. 1-3. Livestock cattle and sheep – production of hides and skins. The numbers of cattle in developed countries is much lower than in developing countries. Due to a much higher slaughtering rate and weight of the cattle, the developed countries produce more hides than developing countries. The numbers of sheep and goats in developed countries is ca. half of the numbers the developing countries have. Skins from sheep and goats from developed countries contribute to 40% of world production. These figures indicate more intensive breeding and slaughtering in developed countries

The worldwide trade in hides, skins and leathers is very often controlled or manipulated by government actions to protect a local leather and shoe industry [7 ,8]. These actions further influence the availability and the price of hides and leathers. A worldwide reduction in the supply of hides and skins in the 1950s also increased the efforts to produce substitutes for leather. Labor and environmental costs caused a shift in the leather and shoe production from industrial countries to developing ones (Fig. 1-5).

The production of shoes is extremely labor intensive. Starting in the 1970s the shoe industry shifted more and more towards countries with low labor costs. Therefore the leather industry moved to these countries too [9, 10] (Fig. 1-6). In addition, government action to improve the environment in industrial countries increased the costs of leather production [6]. Many tanneries either relocated or went bankrupt. Only a few tanneries with a high level of technology remained in countries like the Netherlands, Sweden, France, Switzerland and Germany.

Nevertheless, industrial countries contribute a major part to the production of hides because they have a higher consumption of shoes and leather goods and less and less production of leather and products made from it.

Goods made from leather have a touch of luxury – therefore only countries with a high average income also have a high consumption of shoes (Fig. 1-7).