DEVELOPMENT OF LEATHER FOR MECHANIC'S WINTER GLOVE

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Carpenter Litho & Prtg. Co., Springfield, O.
200 - 7 February 1955

Approved for Public Release
FOREWORD

This report was prepared by the University of Cincinnati, under USAF Contract No. AF 33(600)-22172. The contract was initiated under Research and Development Order No. 612-11, "Coated Air Force Fabrics," and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt Robert Lichtman and Mr. Harold H. Brandt acting as project engineers.

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ABSTRACT

A comparison of the properties desired in glove leather tannages for a comfortable mechanic's winter glove was made. The data collected indicate that irrespective of tannage the leather has a high rate of oil absorption.

The application of various impregnants to glove leather gave an improvement in oil resistance. Some of the impregnants were very oil resistant but did not penetrate into the leather. Using such impregnants as finish films on the leather would give oil resistance but when the finishes were abraded through, the leather would offer very little oil resistance. The data obtained indicate that it is possible to prepare a glove leather for winter mechanic's wear which will have good resistance to oil absorption without materially reducing the desirable properties inherent in glove leather.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research
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INTRODUCTION

DEVELOPMENT OF LEATHER FOR MECHANIC'S WINTER GLOVE

Leather has many excellent properties to recommend it's use as a gloving material. One of the most valuable properties is the insulation it affords. Unfortunately leather also absorbs oils and greases readily. With this absorption of oils and greases the insulating value of the leather is greatly reduced.

The object of this project was the development of a leather for use as a mechanic's winter glove which would have low oil absorption and yet retain as many of the desirable properties of leather as possible. No information was available in the leather literature pertaining to this type of glove leather.

Since there has been little work done to determine the properties of water absorption, oil absorption, water vapor transpiration and flexibility at low temperature of leather used in gloves it was necessary to do some preliminary work to establish values for these properties. Also there were no test methods for some of the properties such as dynamic water vapor transpiration and dynamic oil absorption and it was necessary to work out these test methods. The establishment of values for leather and testing procedures comprise Section I of this report.

Treatment of leather to improve its water resistance has been reported by Cheronis and co-workers (1) and by Cranker and Jorzak (2). Treatment of leather to improve its abrasive resistance has been reported by Oehler and Kilduff (3). No information was found in the literature concerning the resistance of glove leather to oil absorption. After the establishment of values and testing procedures work was done on impregnating the leather to improve its resistance to oil. The results of the impregnation experiments and evaluation of the leathers produced comprise Section II of this report.
SECTION I

PHYSICAL PROPERTIES OF LEATHER FOR MECHANIC'S WINTER GLOVE

To establish the properties desired in leather to be used for the mechanic's winter glove it was necessary to run physical tests designated as being specific for the wear conditions under which the leather would be used. A leather was desired which had a high degree of water vapor transpiration, negligible machine oil absorption, good abrasive resistance, good flexibility at -40°F, normal to good stitch tear resistance and resistance to blocking at 160°F.

Little information was found in the leather literature pertaining to the physical characteristics required of the glove leather to be developed. To obtain this information it became necessary to develop techniques of measuring some of the properties specified such as a dynamic test for water vapor transpiration, a suitable test method for measuring flexibility at low temperature and a dynamic oil absorption test. The other test methods for measuring abrasive resistance, stitch tear resistance, water absorption and resistance to blocking were available.

Test Methods

Abrasive resistance, stitch tear strength and water absorption were run following the test methods in KK-L-311, Federal Specification for Leather and Leather Products (4). The other test methods used were developed and are given below.

Dynamic Water Vapor Transpiration

For the test an aluminum cup developed by Kanagy and Vickers (5) was used. Ten milliliters of water were placed in the cup and then enough absorbent cotton to absorb the water was packed into the cup. The cotton was packed in such a manner that it would not come in contact with the leather specimen.

A specimen of leather was cut large enough to fit over the cup. A bolt was passed through the center of the specimen. By means of washers and a nut, the connection through the specimen was made air tight. The specimen was placed on the cup and a template with a hole through the center was placed over the bolt. Molten wax was then poured into the groove formed by the template and the flange of the cup making an air tight seal. The cup was allowed to stand for thirty minutes to permit equilibrium to be established. The assembly was then weighed and the specimen was flexed for two hours on a flexing machine at 58 flexes per minute. The assembly was removed and again weighed. From the loss in weight and the area of the specimen, which was 25 sq. cm., the water vapor transpiration per square meter per 24 hours was calculated.
Dynamic Oil Absorption

For dynamic oil absorption tests a specimen 4 by 4.5 inches was used. The specimen was weighed and then placed in the Maeser water penetration machine (6) with the grain side up. Into the trough formed by the specimen 20 milliliters of S.A.E. 40 weight motor oil was placed. The 40 weight oil was used because it has approximately the same viscosity at room temperature that 20 weight oil has at 32°F. The specimen was flexed for thirty minutes. Then the specimen was removed from the machine and the excess oil removed by wiping with a towel. The specimen was again weighed and from the increase in weight the percent of oil absorbed was calculated.

Flexibility

The Tinius-Olsen stiffness tester was used to determine the flexibility. A specimen 1 by 2 inches was placed in the machine. No weight was placed on the machine. The specimen was bent through an angle of 90 degrees and the load reading taken on the scale. The specimen was placed in the deep freeze at -15°F for twenty-four hours. The specimen was then removed from the deep freeze and the flexibility determined as rapidly as possible.

Sampling Procedure

From the sides of leather to be tested samples of leather were cut measuring 10.5 by 6.5 inches. The samples were then subjected to various impregnation treatments after which specimens were cut from each sample for the physical tests listed above. The remainder of each sample was ground in a Wiley Mill for chemical analyses. The leathers used were commercial and laboratory tanned 2 to 2-1/2 ounce glove leathers.

Experimental Results

The results of the water absorption tests are given in Table I. The water absorption was determined for a period of 24 hours. There is little difference in the absorption for the chrome, vegetable and sulfonyl chloride horsehide. The vegetable-formaldehyde tanned horsehide has considerably higher absorption values.

The oil absorption values are given in Table II. The vegetable horsehide specimens were run by a static method. In this method the specimen was weighed and then immersed in oil for thirty minutes. The excess oil was wiped off and again the specimen was weighed. From the increase in weight the percent of oil absorbed was calculated.

The chrome, sulfonyl chloride and vegetable-formaldehyde tanned horsehides were tested by the dynamic method. All of the values are high. The chrome tanned horsehide absorbed less oil than the other two tannages. The specimens which were tested by the dynamic method were easily penetrated by the oil mixture within a few minutes of flexing.
The values for the water vapor transpiration are given in Table III. The vegetable and chrome tanned leathers were run by the method of Kanagy and Vickers (5). The sulfonyl chloride and vegetable-formaldehyde leathers were run by the dynamic method developed in this laboratory. All of the values indicate that the leathers are very permeable.

The abrasive index values are given in Table IV. The specimens were run on a modified version of the Bureau of Standards Rubber Abrasion Machine. This machine consists of a cylinder, 8 inches in diameter and 14 inches in length, which rotates at 29 revolutions per minute. The abrasive material, No. 50, silicon carbide cloth, is placed around the cylinder. Four arms extend over the cylinder and 1 square inch specimens are glued to the arms. The arms are weighted so that the specimen is under a pressure of 2-1/2 pounds per square inch. The specimens ride on the top curvature of the cylinder.

The thickness of the specimen was measured, both before and after abrasion, with a Randall-Stickney Thickness Gauge. The specimen was abraded until approximately 50 percent of the thickness was abraded away. The specimens were stationary throughout the test, the abrasive material revolving against the stationary leather.

On this machine one-tenth of an inch wear per 600 cycles was taken as a standard and given the value of 100. From the number of cycles and the wear the abrasive index was calculated.

The stitch tear values are given in Table V. The values are all very good for light leathers. The vegetable-formaldehyde tanned leather is the lowest but still at an acceptable level.

The results of flexibility measurements are given in Table VI. These specimens show a decrease in flexibility with a decrease in temperature. However, the decrease is not serious.

Table VII gives the grease content and pH values of chrome and vegetable tanned leathers. They are typical of commercial tanned leathers.

SECTION II

IMPREGNATION OF LEATHER TO IMPROVE RESISTANCE TO OIL ABSORPTION

As the commercial glove leathers available readily absorbed oil it appeared that impregnating the leather with materials which were resistant to oils would be the best method of improving the resistance of the leather to oil absorption. It was also desirable, if possible, to use an impregnant which would be unaffected by gasoline or other solvents with which it might come in contact when the leather was used in a mechanic's glove.
A series of impregnation experiments was conducted using synthetic resins which were resistant to oil and insoluble in gasoline and other common solvents. The impregnants used and the methods of application to the leather are given below.

**Impregnations Used**

As tannage was to be considered as an approach to obtain the desired results, chrome, vegetable, and sulfonyl chloride tannages were impregnated. As indicated in Section I the tannage of itself did not offer any noticeable improvement in resistance to oil absorption.

**Polyisobutylene**

Polyisobutylene was used to impregnate chrome cowhide leather. The samples were weighed and then immersed in a dilute solution of polyisobutylene in white gasoline. The samples were then allowed to dry and were weighed again. The increase in weight divided by the original weight was used to calculate the percent uptake of the impregnant.

**Vinylite**

Samples of chrome cowhide; chrome, vegetable, and sulfonyl chloride tanned horshide were impregnated with Vinylite, produced by Carbide and Carbon Chemical Company. Before impregnation all of the samples were degreased with chloroform as it was found that the impregnant would not penetrate leather which contained any appreciable amount of greases.

As Vinylite by itself would give a stiff leather it was necessary to use a plasticizer in the impregnating solution. A 10 percent solution of Vinylite was used and the dibutyl phthalate was added at levels of 30 – 50 percent on the weight of the Vinylite.

**Neoprene**

Samples of vegetable and sulfonyl chloride tanned horshide leather were impregnated with neoprene. The neoprene was very sparingly soluble in dioxane and it was necessary to reflux the neoprene in dioxane in order to prepare the solution. The leather samples were also degreased before impregnation. The neoprene was cured by wiping the leather with a 1 percent solution of potassium hydroxide.

**Polythene**

Samples of sulfonyl chloride tanned horshide were impregnated using polythene. Polythene is one of the grades of polyethylene. The polythene was dissolved in benzene for the impregnation. It was not necessary to degrease the leather as the impregnant would penetrate the samples with the grease in them.
Hypalon

Samples of chrome tanned cowhide, horsehide and calfskin were impregnated using Hypalon which is the trade-name of chlorosulfonated polyethylene produced by du Pont. The Hypalon is readily soluble in benzene up to a concentration of 25 percent. However the higher concentrations are very viscous. In the impregnation, solutions of 5 and 10 percent were used. The samples were not degreased but the calfskin which had the lowest grease content, only 10 percent, gave the best results.

When the samples were impregnated they were run through a wringer to remove the excess solution from the surface of the leather. The removal of the solution in this manner prevented the formation of a film on the leather surface, which would cause blocking.

Experimental Results

The percent of uptake of the various impregnants by the leather samples is given in Table VIII. The samples were weighed both before and after impregnation and the increase in weight divided by the original weight was used to calculate the percent uptake of the impregnant. No effort was made to control the percent uptake.

The percent of water absorbed per 24 hours is given in Table IX. The values are all high and there was little if any improvement due to the impregnation in most cases.

The percent of oil absorbed under dynamic flexing for thirty minutes is given in Table X. Examination of the data shows variation in the untreated samples as well as the impregnated samples. The data are presented in graph form in Figure I to show how the oil resistance is influenced by the percent uptake of the impregnant.

Examination of the graphs for the chrome cowhide leather shows that the untreated samples of the leather used for the polyisobutylene treatment and the Vynilite treatment have similar oil absorption. The untreated sample of chrome cowhide treated with the Hypalon was a more oil resistant leather. In all cases the impregnants improved the oil resistance.

The chrome horsehide which was treated with the Vynilite had a finish which was destroyed during the grease extraction prior to impregnation. As shown in the graph in Figure I the finish gave the leather good oil resistance allowing only 7.2 percent oil absorption. When the finish was removed the treatment with Vynilite gave a leather which had less oil resistance. The chrome horsehide treated with Hypalon had good oil resistance. The graph shows that the untreated leather was also resistant to oil being similar to the chrome cowhide used for impregnation with Hypalon.

The chrome calfskin like the chrome cowhide and chrome horsehide in the untreated condition had about the same oil resistance. Treatment with Hypalon improved the oil resistance.
The samples of vegetable tanned horsehide in the untreated condition are similar as to oil resistance. Impregnation with neoprene or vinylite shows an improvement in oil resistance. As shown in the graph one sample of the neoprene leather is very abnormal as to oil resistance. This condition was most likely due to an imperfection in the hide structure rather than on excess uptake reversing the oil resistance. Small imperfections in the hide structure are most likely responsible for the oil resistance showing the variation which occurs in all treatments.

The sulfonyle chloride tanned horsehide leather had poor oil resistance as shown by the graphs in Figure I. Impregnations with neoprene, vinylite and polyethylene improve the oil resistance in each case.

The water vapor transpiration rates are given in Table XI. The transpiration rates are lowered in each case by the impregnation. Hypalon seems to give the greatest amount of lowering.

The results of the flexibility measurements are given in Table XII. Because the presence of grease in the leather caused a slight stiffening effect at 150°F as shown in Table VI the control samples were degreased before test to eliminate the influence of grease. The impregnated leathers were stiffer than the controls in most cases. The impregnants had little influence on the flexibility of the leathers at -150°F even in the case of the leathers treated with Hypalon which were not degreased before impregnation.

The results obtained on the blocking tests are given in Table XIII. The samples were tested for blocking by placing grain surfaces together under a half pound weight for twenty four hours at 160°F. This one half pound weight gave a pressure of 0.5 pounds per square inch. None of the samples showed any heavy blocking except the cowhide which had been impregnated with Hypalon. The vegetable horsehide leather which had been impregnated with neoprene showed slight blocking. One specimen of the sulfonyle chloride tanned leather showed slight blocking. None of the specimens of chrome calfskin leather which had been impregnated with Hypalon showed any blocking at 160°F.

The thermal conductivity was measured using equipment from Central Scientific Company in which the leather specimen is placed between an upper vessel kept at constant temperature and a lower insulated block of copper of known thermal conductivity and mass. The heat conducted through the leather raises the temperature of the copper block by a measured amount. Thermocouples and a galvanometer are used to measure temperature differences. From the rate at which heat is conducted through the leather, the area, thickness and temperature differences of the surfaces of the leather, its thermal conductivity is measured. These values are reported as K-values in Table XIV. There was no difference between the untreated control and the impregnated specimens.
It was desirable to be able to analyze a solution of Hypalon which had been used for impregnation of leather in order to determine how much of the Hypalon had been exhausted from the solution. The following procedure has been worked out and applies both to sulfated and raw oil.

For the analysis a solution with known concentration of Hypalon in benzene was prepared. The percent of Hypalon in the pure solution was determined by weighing about 10 grams into a tared weighing bottle. The bottle was placed in an oven for four hours at 80° - 90°C. The bottle was placed in a desiccator and again weighed. From the weight of the sample and the weight of the Hypalon in the bottle the percent of Hypalon in the solution was calculated.

For the determination of Hypalon in a solution which also contained raw oil, as a solution would if it had been used to impregnate leather, a sample was weighed into a 160 milliliter beaker. Raw neatsfoot oil was then weighed into the solution. The solution of Hypalon and oil was mixed thoroughly. The solution was evaporated almost to dryness on a hot plate. Approximately 10 milliliters of acetone were then added to the beaker. The curd which was formed was kneaded thoroughly. The acetone was decanted off into a tared Gooch crucible, the curd being retained in the beaker. To the curd 100 milliliters of acetone were added and the curd again kneaded. The acetone was again decanted into the Gooch crucible. This washing was repeated at least three times or until the curd was white. With the last washing the curd was removed to the Gooch crucible.

The crucible was dried for 4 hours in an oven at 80° - 90°C. After cooling in a desiccator the Gooch crucible was again weighed; the increase in weight representing the weight of Hypalon in the original solution. From the weight of the Hypalon and the weight of the original solution the percent of Hypalon in the original solution is calculated. The results of such an analysis are given in Table XV. The results show close agreement with the control.

A procedure has been worked out for the analysis of Hypalon in leathers. Samples of leather which had been impregnated with Hypalon were ground in a Wiley Mill. Fifteen grams of the ground leather were weighed into an extraction thimble. The sample was extracted on a hot plate for 8 hours using acetone as the solvent. This solvent extracted the grease from the leather.

The samples were again extracted for 8 hours using benzene as a solvent. The solvent was evaporated from the extraction flask and then the flask was dried for 4 hours in an oven at 80° - 90°C. The results obtained are given in Table XVI. The calculated percent of Hypalon put into the leather was determined by weighing the samples of leather before and after impregnation on a laboratory balance with a low degree of precision while in the analysis an analytical balance was used. This is most likely responsible for the lack of agreement. However more work needs to be done to determine the conditions for this analysis, such as the length of time for the extraction with benzene.
Summary

Specimens of chrome cowhide, chrome-vegetable and sulfonyle chloride tanned horsehide leather have been analyzed for various physical properties.

Leathers have been impregnated with various synthetic resins and analyzed for physical properties.

A method has been developed for determining the amount of Hypalon in solution with oils.

A method has been developed for the determination of Hypalon in leather.

SECTION III
CONCLUSIONS AND RECOMMENDATIONS

The various impregnants gave an improvement in the oil resistant property of leather. Vinylite gave good oil resistance to leather impregnated with it. However vinylite has to be plasticized and the plasticizer can be removed by solvents leaving the leather stiff.

Neoprene also gave good oil resistance. The neoprene was only sparingly soluble and difficult to cure. Also the penetration was not too good.

Hypalon gave good oil resistance to leather impregnated with it. It also was possible to impregnate leather with Hypalon without degreasing the leather. The Hypalon was not extracted from the leather by gasoline and other aliphatic solvents. The Hypalon did not need a plasticizer. Hypalon penetrated the leather the best and gave the best results when the leather had a low grease content.

Chrome tanned cowhide and horsehide glove leathers which have been impregnated with Hypalon have excellent oil resistant properties when tested by laboratory methods. Since leathers with a low grease content seem to absorb the Hypalon impregnant more readily, leather which has a grease content of not more than 10 percent on a dry basis should be obtained and impregnated to approximately a 10 percent uptake of Hypalon and tested under service conditions.
BIBLIOGRAPHY


### TABLE I

**WATER ABSORPTION**

Per Cent Water Absorbed per 24 Hours

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### TABLE II

**OIL ABSORPTION**

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### TABLE III

**WATER VAPOR TRANSPARATION**

Grams per Square Meter per 24 Hours

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### Table VI

**FLEXIBILITY**

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WADC TR 514-63 12
## TABLE VIII

**PER CENT UPTAKE OF IMPREGNANTS**

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### Sulfonyl Chloride Horsehide

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WADC TR 54-63  13
### TABLE IX

**WATER ABSORPTION**

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### TABLE X

**OIL ABSORPTION**

**Per Cent Absorbed in 30 Minutes**

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WADC TR 51-63

Approved for Public Release
### TABLE XI

**WATER VAPOR TRANSPERSION**

Grams Per Square Meter Per 24 Hours

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WADC TR 54-63  15
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### TABLE XIII

**BLOCKING AT 160°F.**

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**HEAT TRANSFER**

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### TABLE XV

**ANALYSES OF HYPALON-OIL MIXTURES**

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### TABLE XVI

**HYPALON IN LEATHER**

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WADC TR 54-63

Approved for Public Release
FIGURE 1

INFLUENCE OF IMPREGNANTS ON OIL RESISTANCE

CHROME COWHIDE

% OIL ABSORBED

% P+4 BUTYLENE % VINYLITE

10 20 30

CHROME HORSEHIDE

% OIL ABSORBED

% VINYLITE % HYPALON

10 20 30

CHROME CALF

% OIL ABSORBED

% HYPALON

10 20 30

VEGETABLE HORSEHIDE

% OIL ABSORBED

% NEOPRENE % VINYLITE

10 20 30

SULFONYL CHLORIDE HORSEHIDE

% OIL ABSORBED

% NEOPRENE % VINYLITE

10 20 30

% POLYTHENE