R58-23

POLYSULFIDE RUBBER TREATMENT FOR GLOVE AND SHOE UPPER LEATHERS*

E. C. Dogliotti, C. W. Mann and J. Barry

QM Research and Engineering Center
Natick, Massachusetts

ABSTRACT

A process is described for treating cowhide glove and similar flexible types of leather with liquid polysulfide polymers to produce a high degree of resistance to penetration or absorption of petroleum products, liquid chemicals, and water. The polymer is applied to the grain layer only and is heat-cured in the usual drying tunnel to form a protective barrier in the leather without serious detraction from the feel or flexibility of the leather or the ability of the flesh side to absorb perspiration. A small-scale tannery trial is described showing the possibility of plant application without difficulty. The results of a field-wear trial of treated leather gloves are presented.

INTRODUCTION

Satisfactory performance of leather in gloves, shoes, and other clothing items is dependent upon a combination of properties, including strength and abrasion resistance for durability, absorption and vapor permeability for comfort, and air space between fibers for insulation. These characteristics of leather in the normal dry state are generally satisfactory, but they may be adversely affected in leather that comes in contact with water or other liquids. The problem dates perhaps to antiquity, but only during the last few years has there been real progress toward a satisfactory solution. Several methods have been described for improving the resistance of leather to absorption or penetration of water (1–4), but much less attention has been given to other liquids.

The exposure of military leather items to gasoline, oil, and other petroleum products ("POL" products in quartermaster terminology) has presented a serious problem, particularly under extreme-cold conditions. For example, there have been instances in which Arctic deerskin mittens have become so saturated with POL products within a few weeks of wear that most of their insulating value was lost and they were a potential fire hazard, especially if in close proximity to an open fire.

*Presented at the Fifty-fourth Annual Meeting, Swampscott, Massachusetts., May 27, 1958.

This paper describes experiments designed to solve the problem by improving the resistance of leather to absorption and penetration of petroleum products, water, and other liquids. A tannery-trial application of an impregnation process is described, as well as the results of laboratory evaluations and a limited wear trial of treated cowhide leather gloves.

EXPERIMENTAL

Surface coatings.—In the exploratory studies for producing a POL-resistant glove leather, attempts were made to develop a treating material which could be easily applied to the grain side of leather to form a liquid-resistant, light but serviceable, plastic-type, surface coating. At the time, this approach appeared to offer the most promise as a solution of the problem, more so than any available impregnating process. It was erroneously assumed from earlier impregnation studies that the desired resistance to POL products could be attained only through the use of large quantities of impregnating materials which would impair leather characteristics such as flexibility.

Various materials were investigated as surface films on horsehide and deerskin glove leather, including acrylates, neoprenes, vinyl or vinylidene chlorides, and various polyethylenes. Laboratory tests showed that coatings less than 10 mils thick provided good resistance to gasoline for more than 10,000 cycles with the Maeser Tester and that the feel and softness of the leather were also acceptable. However, surface coatings of this type were too stiff for use at low temperatures and lacked durability. For example, in one wearing trial 10 pairs of leather gloves were coated to approximately 8 mils thickness with a promising polyvinylidene chloride and butadiene-acrylonitrile mixture and worn by workmen engaged in normal handling operations involving gasoline and other POL products. Within three days, scuffing and peeling of the gloves had become so bad that the gloves offered no better resistance than the untreated controls.

Impregnation.—The unsuccessful experiments with surface films led to a re-evaluation and study of impregnation processes and materials. Screening and application studies were performed on a number of potential impregnating agents such as epoxy resins, acrylates, liquid polysulfide polymers, polyethylenes, and special oils, greases, or waxes. Of the materials investigated, the ones that showed greatest promise were the liquid polysulfide polymers. These liquid, low-molecular-weight, polymercaptan polymers are capable of further polymerization into rubber-like elastomers with unusually high resistance to oils and solvents and with good aging and low temperature properties.

Although commercial methods for applying the liquid polysulfide polymers to leather have been described in this journal (5) and in technical bulletins

(6), their principal application apparently has been in packings, belting, and other mechanical leathers. These commercial methods use a process of total immersion and thorough impregnation of the leather. These processes proved to be unsatisfactory for glove or shoe upper leather, nor could any satisfactory method based on thorough impregnation be developed in the present work by which leather could be obtained with good liquid resistance and without loss of desired leather characteristics.

During some exploratory work on emulsions of the polysulfide polymers, in which morpholine was employed in the dual capacity of emulsifier and amine curing agent, it was found that these emulsions could be applied directly to the grain side of the leather by brushing or rolling to produce a leather of fair liquid resistance and good leather characteristics. Further work with solutions composed of the polysulfide polymer blended with morpholine as the curing agent and solvents such as toluene, perchloroethylene, and finally tetrahydrofurfuryl alcohol proved to be even more effective.

POLYSULFIDE POLYMER TREATMENT

In essence, the treatment consists of applying a polysulfide solution to the grain surface of the leather in a manner similar to hand-swabbing. Immediately following the application, the leather is heated at 140°–160°F. in a chamber or drying tunnel with good air circulation for 15–60 minutes and then placed in a dry loft at approximately 90°–100°F. for 16–24 hours. The treatment produces a permanently fixed, flexible, polymeric layer within the leather approximately 10–15 mils thick and extending from the grain surface inward. This treated leather is capable of effectively resisting penetration by liquids such as water, POL products, and certain corrosive chemical solutions. The flesh side of the leather remains unaffected by the treatment and, hence, retains its comfortable feel and perspiration-absorption properties. Furthermore, the treatment has only a slight effect upon strength or other leather characteristics.

The treating materials and some of their physical properties are shown in Table I.

The liquid polysulfide polymer Thiokol LP-32 was found to produce leather of good liquid resistance and best over-all leather characteristics compared to other liquid polysulfide polymers and blends. This product is supplied in the form of a viscous liquid which must be diluted with a solvent for satisfactory penetration into leather. Both morpholine and tetrahydrofurfuryl alcohol (THFA) serve in a dual capacity: morpholine as an amine curing agent, THFA as a copolymerizing agent, and both materials as diluents. Oleic acid, a retarding agent, has been found useful in many cases in facilitating penetration and improving the distribution of the polymer within the leather.

TABLE I

TREATING MATERIALS AND THEIR PHYSICAL CHARACTERISTICS

(Information from manufacturers' bulletins)

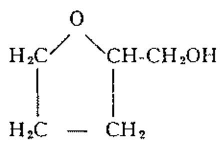
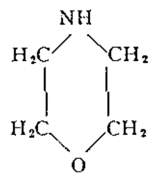
Physical Characteristics	Polymer Thiokol LP-32 (Thiokol Corp.)	Tetrahydrofurfuryl-alcohol (Quaker Oats Co.)	Morpholine
Structure	(HS-R-SH)*n*		
Approx. molecular weight	4,000	102	87
Specific gravity	1.27(20°/4°C.)	1.05(20°/20°C.)	1.00(20°/20°C.)
Vapor pressure, mm. Hg	Very low	2.3(41.6°C.)	8(20°C.)
Viscosity, poises	350-450(25°C.)	0.062(20°C.)	0.023(20°C.)
Flash point, °F.	455	183	100

TABLE II

TREATING SOLUTIONS

Materials (parts by weight)	Solution A	Solution B
Thiokol LP-32	100	100
Tetrahydrofurfuryl alcohol	45	75
Morpholine	10	
Oleic acid	0.5	
PHYSICAL PROPERTIES		
Specific gravity, 78°F.	1.15	1.16
Viscosity, centipoises, 78°F.	880	710
pH (water extract)	9.5	7.3
Flash point, open cup, °F.	170	169

Table II shows the composition of two treating solutions which have consistently produced good results, especially with cowhide glove or garment leathers.

In Solution A, morpholine, which was used in many of the earlier formulations on glove leather, is employed instead of some of the more reactive amine or paint drier-type curing agents, e.g., diethylamine or cobalt hexogen. Morpholine has several important advantages: not only is it sufficiently effective for this treatment but it is easily removed by heat during the curing process, causes no apparent damage to leather, and is available and already in use within the leather industry.

During our studies with THFA as a solvent it was found that this material is capable of copolymerizing with some of the liquid polysulfide polymers. The reaction may be similar to that described in the literature for furfural (6), although considerably slower in rate. Solution B contains only the polysulfide polymer and THFA. This solution has several advantages over Solution A, being simpler in composition, penetrating more quickly, and generally providing greater resistance in the treated leather. However, certain types of leather, containing resins or other material that apparently act as anticatalysts, require morpholine for an effective treatment. In these cases Solution A should be used.

The most convenient methods of application, on a laboratory scale, were by rolling with a paint roller, brushing, or swabbing pieces of leather approximately 1 square foot in size. Whole sides were easily treated in the same way. Usually the treated leather was placed within 5 minutes into a drying cabinet with rapid air circulation at 140°–160°F. for one hour (Solution A) or 15 minutes (Solution B). The leather was then maintained at 90°–100°F. overnight for further curing and removal of the residual solvents.

Preliminary application of the polymer to finished commercial garment leather was ineffective in areas containing a high concentration of oil. In order to eliminate this difficulty subsequent laboratory tests and tannery trials were made on degreased leather.

During the first tannery experiment 10 sides of cowhide glove leather were treated by swabbing with a solution containing 30 parts morpholine to 100 parts polysulfide polymer. Although room temperature on the day of the experiment was low, the highly viscous formulation penetrated readily in most places, imparting good resistance to penetration of water and POL products, but it failed to produce this effect uniformly over the entire area of the sides.

A second tannery trial was made on 15 sides of cowhide glove leather in order to evaluate a spray formulation consisting of polysulfide polymer, morpholine, and perchloroethylene. In this trial the liquid resistance of the leather was relatively low and very spotty over all of the sides. Weight measurements of the treated leather showed that material losses were approximately 50%, which shows why the poor results might have been expected.

A third tannery trial comprising 30 sides of degreased cowhide glove leather proved more successful than previous trials. Solution B of Table II was applied to the grain side of the leather, using a mohair paint roller to spread the solution quickly and uniformly. The amount of solution applied was calculated so as to impart 18 grams of polymer, or approximately one ounce of solution, per square foot of leather. After treatment the sides were hung in a drying tunnel at 140°–160°F. for 15 minutes and then overnight in a dry loft at approximately 90°F. The dried leather was washed for 20 minutes in a drum at 125°F., fatliquored with 4% oil, dried, and staked.

EVALUATION OF TREATED LEATHER

The effect of polysulfide polymer concentration on water resistance was determined on 5 sides of degreased cowhide glove leather. Single pieces from each side were treated to contain 9, 12, 15, 18, 21, and 24 grams polymer per square foot of leather. The leather was washed, fatliquored, dried, and staked after treatment. Resistance to water penetration was measured by the QM Tap Tester (7) using a ½-lb. load. Figure 1 shows the number of cycles required for initial water penetration.

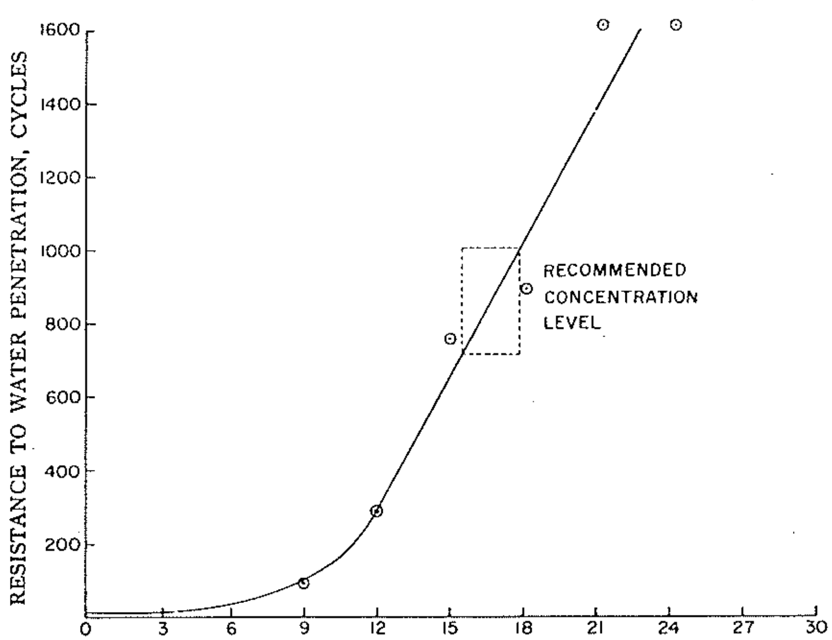


FIGURE 1.—Water resistance for cowhide glove leather at different polymer concentration.

Resistance to water penetration increases with increasing concentration of the polymer from approximately 20 cycles for untreated leather to 1600 cycles for leather treated at the 24-gram level. No other treatment except a Bavon process (8) provided a similar high resistance to water penetration. The increase in resistance is directly proportional to the polymer concentration within the range of 9 to 24 grams. Also indicated in Fig. 1 is the recommended concentration level for glove leather which is 15 to 18 grams polymer per square foot of leather. This suggested level was selected on the basis of a combination of properties, including water- and POL-resistance and other characteristics related to comfort and performance in gloves. Higher treating levels provided greater water resistance but at a sacrifice in water vapor permeability and softness as well as adding to the cost and also to the weight of the gloves.

Because of the inherent difference in hide structure in different areas of a hide, some variation in properties is unavoidable. The effects of this variation were studied on ten of the sides treated in the third tannery trial previously described. Results of the tapping test for these leathers are presented in Table III.

TABLE III

VARIATION IN WATER RESISTANCE IN A LOT OF TANNERY-TREATED SIDES OF COWHIDE GLOVE LEATHER

Location on Side	Number of Measurements (2 for each area)			
	Below 100 Cycles	100-299 Cycles	300-599 Cycles	Above 600 Cycles
Backbone-tail	0	3	10	7
Backbone-center	1	4	5	10
Belly-center	2	4	4	10
Shoulder	2	10	3	5
Total	5	21	22	32
Side number				
1	4	3	1	0
2	0	5	1	2
3	1	2	3	2
4	0	3	4	1
5	0	2	5	1
6	0	2	2	4
7	0	1	3	4
8	0	2	1	5
9	0	1	2	5
10	0	0	0	8

The results in the upper part of the table show that 32 of the 90 measurements did not produce a leak in 600 cycles, thus indicating a relatively high degree of water resistance. Only 5 values fell below the 100-cycle level, the lowest value being 71 cycles. Resistance was generally least in the shoulder area as compared to the other areas tested. The table also shows the variation in results for treated sides in the same lot. The results were uniformly high on eight of the sides, whereas the other two showed a significant difference in water resistance. The poorest side was No. 1 with four values below 100 cycles compared to only one similar value for all other sides. The highest degree of water resistance in the lot was that of side No. 10, which did not leak in any test.

Another method of measuring water resistance was used to compare polysulfide-treated cowhide glove leather with military glove-shell leather (untreated horsehide) and acrylate-treated horsehide glove leather. Technologists wore gloves or mittens fabricated from the leather for handling wet bricks, lifting, turning, and stacking them from a resting position in approximately 1 inch of water. Figure 2 shows the time required for initial water penetration as well as the rates of water absorption during the test.

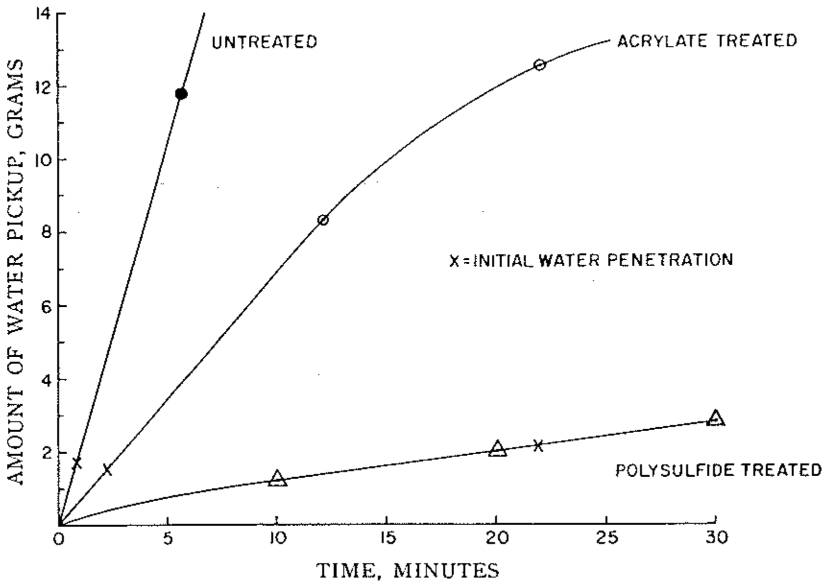


FIGURE 2.—Wet brick test for water resistance of gloves.

The initial water penetration or feeling of wetness was noticed by the technologist in approximately 30 seconds for untreated leather, 1.5 minutes for acrylate-treated leather and 22 minutes for polysulfide-treated leather. Differences in water resistance are also shown by the rates of absorption. In less than 10 minutes palm areas of the untreated or acrylate-treated leather were saturated with water. In contrast, the polysulfide-treated leather retained its dry feel after 30 minutes, except in small areas of the palm where the leather had been squeezed tightly against the wet bricks. It also was comparable or superior to untreated leather in other properties, such as drying time and flexibility after soaking.

Since no standard method was available for measuring resistance of leather to POL products, it was necessary to devise a suitable laboratory procedure. Guided by experience in water-resistance testing, initial trials were made using the Maeser Dynamic Flex Test, in which the leather specimen was mounted grain side up, forming a trough to contain kerosene. This method proved to be unsatisfactory for glove leather as it did not apply sufficient strain to the leather fibers to force kerosene through treated leather or leather coated with a repellent surface film. For example, specimens that showed resistance to penetration for several thousand cycles in this test sometimes were penetrated by kerosene in less than 1 minute of rubbing with a finger under moderate pressure. A test procedure was devised for measuring the time required for penetration of gasoline through a leather specimen rubbed with a rubber-covered finger. The specimen is placed grain side up on a paper towel resting on a flat surface. Approximately 1 ml. of gasoline is poured onto the grain surface and rubbed vigorously with the rough surface of the rubber finger. The specimen is lifted after 30 seconds, 1 minute, and 2 minutes to see if penetration and staining of the absorbent paper has occurred. The penetration times and corresponding ratings are as follows:

Penetration time (minutes)	Rating
Below 0.5	Poor
0.5 to 1.0	Fair
1.0 to 2.0	Good
Above 2.0	Excellent

When polysulfide-treated pieces containing 9 to 24 grams polymer per square foot of leather, referred to in Fig. 1, were tested for gasoline resistance, they rated excellent over their entire area after impregnation at the 15-gram level or higher. Excellent ratings also were obtained on the 10 tannery-treated sides referred to in Table III.

The POL resistance of polysulfide-treated cowhide glove leather also was evaluated in a field-wear test comparing treated and untreated leather mittens. The mittens were worn over wool inserts on a specially constructed POL material handling course, in which test subjects performed operations such as filling a 5-gallon can from a large oil drum and wiping off spillage with rags saturated with gasoline. Tests were conducted over a period of 22 days at temperatures as low as minus 31°F. Both mittens and inserts were weighed at intervals during the test to determine the petroleum pickup shown in Table IV.

As Table IV shows, the average pickup was 101 grams for untreated mittens compared to 54 grams for the treated mates that were worn for a much longer period. Many of the untreated mittens developed failures during the wear

TABLE IV

FIELD WEAR TRIAL OF TREATED VS. UNTREATED MITTENS
PETROLEUM PICKUP DURING HANDLING OPERATIONS

(Average values)

Mitten	Number of Mittens	Number of Traversals	Original Weight of Mitten Insert, grams	Petroleum Pickup after Test Completion (Mitten and Insert), grams	Petroleum Pickup per Traversal, grams
Treated	24	74	174	54	0.73
Untreated	24	52	168	101	1.94

period and were replaced with nontest mittens to complete the test of the treated mates. The untreated mittens absorbed petroleum products at a rate nearly three times that of the treated ones. At the conclusion of the test the subjects commented favorably on the relatively dry condition of the treated mittens as compared to the poor feel and appearance of the untreated ones. Only the treated mittens were considered satisfactory for resisting petroleum products, although both types were considered adequate in gripping characteristics and hand dexterity.

The maximum amount of polysulfide polymer that may be used satisfactorily without adversely affecting glove leather is determined largely by the effect of the treatment on flexibility. A measure of this effect is the force required to bend a specimen through an angle of 20 degrees, using the Tinius-Olsen Stiffness Tester. The common single-layer specimen of glove leather proved to be too flexible, but a 3″ x 4″ specimen folded and fastened in a four-layer thickness provided a satisfactory measurement. A comparison of polysulfide-treated glove leather with the standard heavy-duty glove leather and with similar commercial extra-heavy-duty glove leather, one ounce thicker than that required in military specifications, is presented in Fig. 3.

Compared to the regular heavy-duty leather, the polysulfide-treated leather containing a polymer concentration of 18 grams per square foot of leather proved to be more flexible at room temperature and at minus 20°F., perhaps because of a lowered concentration and more uniform distribution of the oils within the treated leather. At minus 40°F. the difference in stiffness is probably not significant. It may be observed that the thicker commercial leather is much stiffer than the other two under all conditions, the difference being very significant at the two lower temperatures.

The effects of polysulfide concentration on stiffness of cowhide glove leather at different temperatures are shown in Fig. 4. Each point on the curves represents the average value obtained on five specimens.

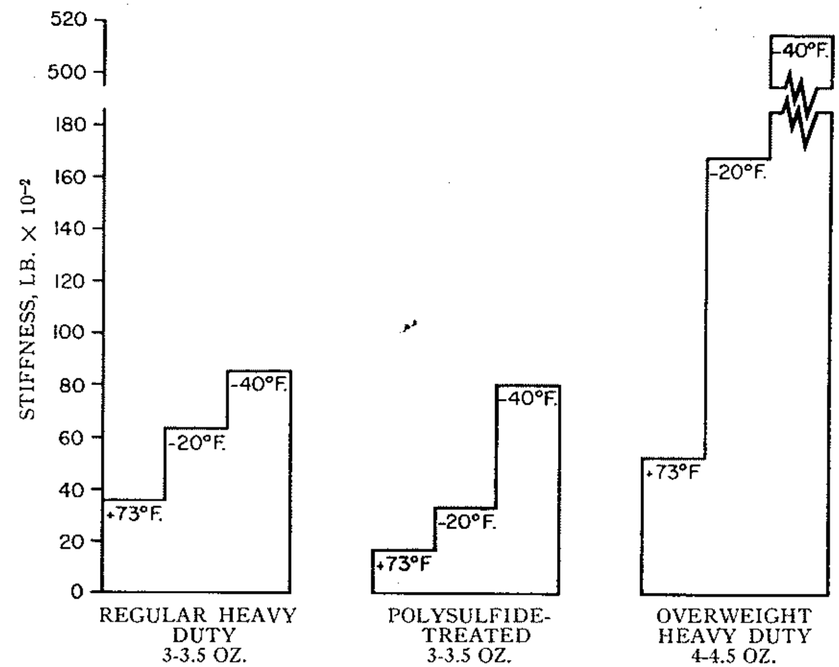


FIGURE 3.—Stiffness for treated and untreated cowhide glove leather vs. temperature.

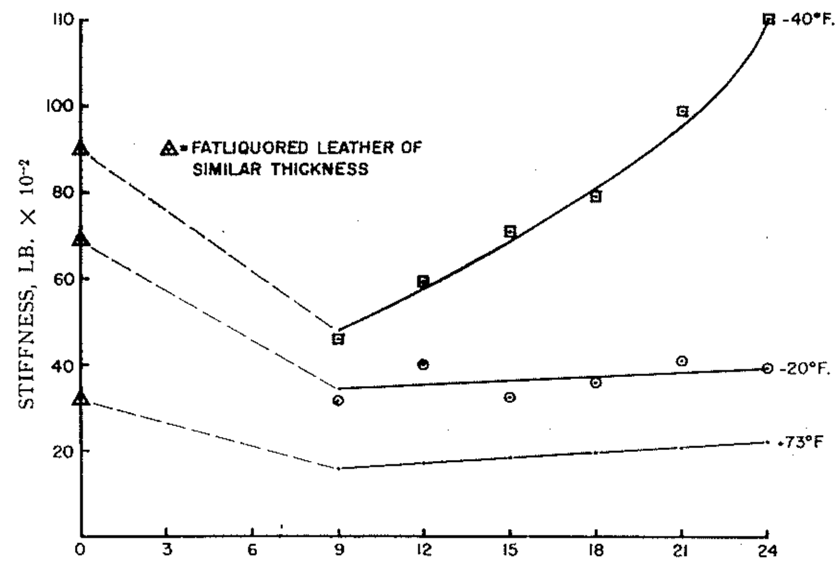


FIGURE 4.—Stiffness for cowhide glove leather at different polymer concentrations vs. temperature.

The results show that the stiffness of the polysulfide-treated leather does not exceed that of untreated leather until the treatment level reaches 21 grams or more. Moreover, low temperatures cause no significant increases in stiffness until minus 40°F. has been reached.

It is generally impossible to determine precisely whether a leather treatment will affect feel or comfort of a glove, but physical properties such as absorption and permeability to water vapor are definitely related to comfort. Leather treated with polysulfide at the 18-gram level absorbs water on the flesh side almost as readily as untreated leather and its permeability to water vapor is approximately 300 g. per square meter in 24 hours. This value is considered to be satisfactory for comfort. Limited wear trials, including the POL-handling test described above, appear to confirm this conclusion.

Water-resistance properties of leather may be adversely affected by leaching or migration of the treating material in storage or use, especially under severe conditions such as repeated wetting and drying. Because of the reaction converting the polysulfide polymer to a more insoluble material, it would be expected to resist migration or washing once the material is deposited in the structure. A test was made to determine the effect of repeated washing on polysulfide-treated leather. Specimens from five sides of tannery-treated cowhide glove leather were laundered 10 times in succession. Each time the leather was washed with laundry soap for 15 minutes at 140°F., rinsed, and then dried at 140°F. for 30 minutes. When the leather was tested afterward, all specimens resisted water penetration for more than 600 cycles and maintained their excellent rating for gasoline penetration.

The polysulfide-treated leather has shown promising results in resisting many different liquid chemicals. For example, the treated cowhide glove leather has been tested for resistance to battery acid (34% sulfuric acid), ethylene glycol, and 2-normal sodium hydroxide solution. In each case 10 grams of liquid were poured onto the grain surface and allowed to stand from 15 to 60 minutes. Comparison of bursting strength measurements for the exposed and adjacent areas showed no loss in strength except exposure for one hour to the sodium hydroxide solution.

DISCUSSION

Application to glove leathers.—The formulations of the treating solution described in Table II and the method of application used in most of the experiments discussed above were satisfactory during laboratory studies and presented no difficulty in the tannery trials. However, changes in the formulations may become necessary in some instances; for example, some leathers contain resinous or synthetic tanning agents that, as mentioned before, tend to act as anticatalysts and require a higher than usual concentration of morpholine for an effective cure.

It was found convenient in this study to follow a standard procedure of degreasing leather prior to treatment in order to eliminate the variable effect of excess oil. Degreasing is not an essential step in the process, however, as the polysulfide treatment has been applied successfully to leather containing more than 10% oil. For regular production of polysulfide-treated leather, a lower oil content is suggested. There are indications that a lower oil concentration provides adequate lubrication with generally more satisfactory results. Leather properties such as density, insulation, feel, and flexibility are adversely affected, especially in cold weather, by large amounts of oils; therefore, any excess should be avoided. A remarkable feature of the polysulfide polymer treatment is its firm fixation within the leather which allows the leather to be processed by regular tannery washing and fatliquoring after the polysulfide treatment without affecting resistance to gasoline or water penetration.

The polysulfide treating materials described in Table II do not present a serious hygienic problem in use, but should be handled in a well-ventilated area using normal precautions. Protective aprons and gloves are recommended to avoid prolonged contact with the skin. The flash point of the treating solutions (approximately 170°F.) indicates that they are not a serious fire hazard.

One objectionable feature found in certain lots of polysulfide-treated leather was an undesirable odor which persisted for several weeks or months despite repeated attempts to eliminate it by heating and washing. In the earlier experiments, most of which were performed on leather from only one tannery, the problem of odor appeared to be a limiting factor in the acceptability of polysulfide-treated leather. Much more favorable results were obtained, however, when the treatment was applied to leather from several other tanneries. These lots did not develop an odor, or in a few cases developed only a slight but acceptable odor. There are indications that the variation in results may be dependent upon the materials used in the fatliquor. In any case, the elimination of the odor appears to be simply a matter of minor changes in materials applied during the tanning or fatliquoring operation.

The polysulfide polymer treatment appears to offer several advantages over other similar processes, particularly with regard to the combination of properties it imparts to glove leather. Since polysulfide polymer-treated cowhide glove leather is capable of resisting water, POL products, and some liquid chemicals, like battery acid, such leather eventually is expected to allow a single multipurpose military glove to be issued.

Experimental applications of the polysulfide polymer to other soft types of leather, such as horsehide, sheepskin, and deerskin, indicate that treatments similar to those applied to cowhide produce good results. Water resistance as high as 600 cycles in the tapping test has been attained as well as excellent resistance to gasoline. However, the relatively loose fiber weave of these types of leather presents a more difficult problem than the more compact structure of cowhide leather; accordingly, they may require a slight change in formulation or a higher treatment level for effective results.

Although most of these applications were made on chrome-tanned leather, the polysulfide treatment has also been applied successfully in a few tests to glove leathers of other tannages, including vegetable and various experimental tannages.

Studies of storage stability are under way on glove leather specimens treated with various solutions, including some in which plasticizers and chain-stopping agents were incorporated. These studies are most important for military items which may be stored for two years or more prior to use. Gloves and leather specimens which were treated over three years ago with some of our initial treating solutions have shown no apparent change in feel or flexibility.

Application to shoe upper leather.—After completion of the major portion of the laboratory work on producing a liquid-resistant cowhide glove leather, efforts were directed toward producing shoe upper leather of similar characteristics. The formulations developed for glove leather, for instance, solutions A and B of Table II, were immediately found less suitable for upper leather. In one preliminary trial, though, the effectiveness of the liquid polysulfide polymer Thiokol LP-32 was demonstrated by carrying out a wading test with a boot that had a rubber sole directly molded to polymer-treated upper leather and the seams all tightly sealed. After seven hours of walking with the lower portion of the boot in water, a technologist found the inside of the boot and sock "bone-dry". Despite this encouraging beginning, further work showed that additional laboratory studies and tannery trials are yet required.

A recent tannery trial was made on 10 sides of corrected-grain, chrome cowhide Army upper leather with what appeared in laboratory tests to be a promising formulation, consisting of 100 parts Thiokol LP-32, 50 parts THFA, and 10 parts morpholine. The dyed but unfinished leather received 30 grams of polymer per square foot, which is considerably more than what was required for glove leather. Application was the same as for Solution A of Table II. The sides of leather were finished by the usual tannery steps and materials without difficulty.

The leather produced in this trial is normal in appearance and feel. It does not have a peculiar odor or any other undesirable features. Its POL resistance is very good, but its water resistance is no more than fair.

Results like these are encouraging, but at the same time they prove that further work is needed. Different tannages produce leather varying greatly in absorptive properties and, therefore, requiring a variety of techniques. Double treatments, for instance, have been tried out on a small scale with considerable success.

ACKNOWLEDGMENT

The authors wish to thank the personnel of the A. C. Lawrence Leather Company, Peabody, Massachusetts, where several pilot-tannery trials were conducted, and especially M. Battles and J. Bassett, for their cooperation. The assistance of Pfc. E. Welch in the performance of the physical tests is also acknowledged.

REFERENCES

1. Somerville, I. C. and Fisher, R. F. M. *JALCA*, **53**, 365 (1958).
2. Hopton, A. W. *JALCA*, **53**, 366 (1958).
3. Cheronis, N. D. *Footwear and Leather Series Report No.* 8, pp. 149–55 (1954), U. S. Department of Commerce.
4. Hunter, M. J., and Dudley, C. F. "Organosilicon Compositions Containing Zirconium Compound and Leather Treated with Same", U. S. Pat. 2,728,736 (1955).
5. Cranker, K. R., and J. S. Jorczak. *JALCA*, **47**, 178 (1952).
6. Technical Bulletin "Thiokol Liquid Polymer LP-3", Thiokol Corporation, Trenton, N.J.
7. Mann, C. W. *JALCA*, **51**, 637 (1956).
8. Person, F. *Leather Mfr.*, March 30 (1957).

Received August 25, 1958.

DISCUSSION

DR. SHU-TUNG TU (United Shoe Machinery Corporation): There are several kinds of polysulfide polymers. My first question is: Could you tell me which one you think is suitable or that you have found satisfactory for glove leather?

The second question is: What is the thickness of the film and what is the penetration of the polymer?

Third, what is the history of the application of the polymer? (This is glove leather.) At what stage do you apply it? Is it chrome-tanned leather? How about the dye application?

MR. MANN: We applied Thiokol LP-32 and found it more satisfactory than other polymers available at the time we started this work. We have not tested those other products exhaustively.

As far as penetration goes, we think we get penetration approximately a third of the way through from the grain side. We know the flesh side absorbs water or perspiration readily, and when we recently made bending tests of the leather at extremely low temperatures, we noticed the position of the break which indicated that the Thiokol penetrated about a third of the thickness.

The treatment is to be applied after the dye. I think you would run into difficulty dyeing this kind of leather. It can be applied to some types of finished leather, although in general that would not be the way the tanner would apply it. It could be applied after fatliquoring, or as we have shown here, you can fatliquor afterward, if it is desirable.

DR. TURLEY (Rohm & Haas Company): Is everything O.K. from the toxicity angle and the question of skin dermatitis and so on? Would it be safe to use?

MR. MANN: The morpholine catalyst in this case is the kind of chemical that you have to be careful with. We would recommend that you take normal precautions in treating. However, I do not think it is extremely dangerous in the low concentration used here. We have not determined toxicity, however.

MR. CASSEL (National Bureau of Standards): I did not understand why odor was not more of a problem. You would expect it to be, but you apparently did not have any problems along this line. Is it because of the uniqueness of this particular Thiokol product?

MR. MANN: No, we think it has to do with the oils that are used in the leather. The first leather we used was a garment type which did cause some difficulty in eliminating odor. However, we had no difficulty with upper leather and no difficulty with certain tannages of glove leather.

DR. MELLON (Eastern Regional Research Laboratory, USDA): Did you attribute the differences you found from side to side to the mechanical treatment of application or to differences in the leather?

MR. MANN: We did not investigate that exhaustively. It probably was due partly to variation in hides. Some hides may be a little more absorptive and require a little more material. However, these men were inexperienced, and it could be partly due to uneven application.

DR. WALLACE WINDUS (Eastern Regional Research Laboratory): These materials are domestically produced, I realize, but the same types of compounds are solid propellants for rockets. I wonder about the availability of them to the leather industry, in an emergency.

MR. MANN: There has been no indication of any shortage whatever. I don't think the same materials are used.

JOSEPH ORIETAS (Albert Trostel & Sons Company): How would such a treatment affect the subsequent finishing of the leather?

MR. MANN: Undoubtedly there will be a problem in applying the normal-type finishes, as with any other water-repellent treatment. The only experience we have had is with one special type of finish, applied not in the normal way but from solvent-type solution. There was no difficulty whatever with that one. That I would not consider a typical finish.