Oct. 15, 1940. J. H. McGILL ET AL 2,217,762

TREATED LEATHER AND PROCESS OF PREPARING

Filed Aug. 9, 1937

Fig.1

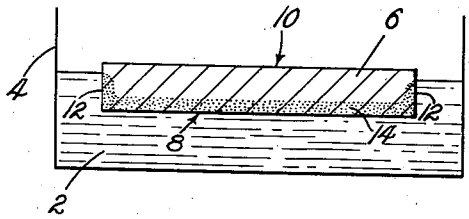



Fig.2

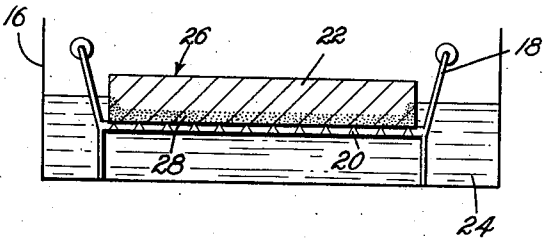



Fig.5

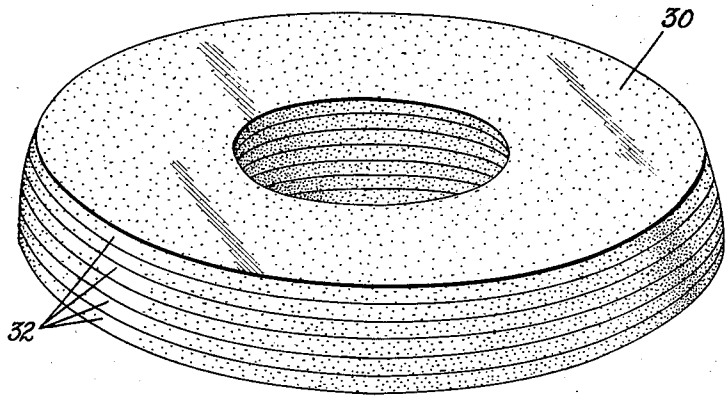



Fig.4

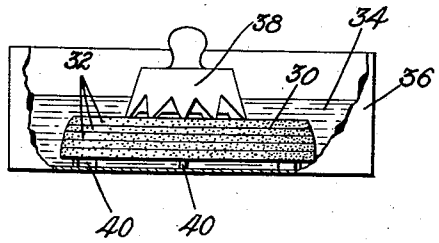
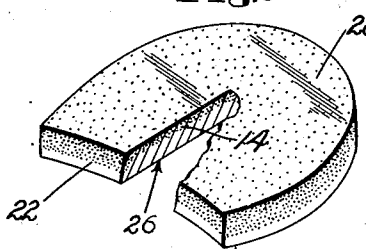



Fig.3




INVENTORS

John H. McGill

Walter H. Wadyer

By their attorney

Victor Cobb

Patented Oct. 15, 1940 2,217,762

# UNITED STATES PATENT OFFICE

2,217,762

## TREATED LEATHER AND PROCESS OF PREPARING

John H. McGill, Winchester and Walter H. Wedger, Belmont, Mass., assignors to B. B. Chemical Co., Boston, Mass., a corporation of Massachusetts

Application August 9, 1937, Serial No. 158,019

1 Claim. (Cl. 149—6)

This invention relates to leather and leather articles having advantageous properties and to methods of preparing the same.

Objects of this invention are to provide leather articles of improved characteristics, including stiffness, wearability, resistance to fraying, and resistance to detanning upon exposure to water, while in other respects having essentially the normal characteristics of leather. Another object is to provide leather articles wherein the flesh side of the leather and adjacent portions are improved in such respects, while preserving the grain side of the leather in its original condition. Other objects are to provide advantageous methods of preparing such articles.

In accordance with the above and other objects, in one aspect of the invention we have provided leather articles wherein said leather is impregnated from the flesh side with sulphur in molten condition and wherein said impregnation has taken place to a predetermined degree approaching but not reaching the grain side thereof. In such leather articles the flesh side of the article remains firm and stiff throughout the life thereof. The invention makes possible the use of so-called "fleshy" leather for many purposes hitherto impossible by reason of the soft, yielding and unsubstantial properties of the flesh side of such leather. As a result of this invention, such leather may be treated to provide properties of firmness and stiffness equal to those of leathers of considerably higher quality. In the case of high quality leather, the invention may be employed greatly to improve the properties of the leather for many purposes.

A highly advantageous application of the above aspect of the invention is in the preparation of detachable heel lifts such as disclosed, for example, in United States Letters Patent No. 1,844,248, granted February 9, 1932, in the names of Frank T. Gentile and Fred Maccarone. In such constructions, a leather heel lift is detachably disposed with the flesh side thereof contiguous to the lift-receiving surface of a wood heel, and the lift is secured to the heel by means of a post extending into and secured in a socket in the heel. When the lift is worn, removal thereof is ordinarily accomplished by first inserting a leverage tool between the flesh side of the lift and the adjacent top-lift-receiving surface of the wood heel. By the present invention, heel lifts may be prepared wherein the flesh side of the leather and adjacent portions are stiffened and hardened, and which lifts, when worn sufficiently for replacement, readily may be pried off the wood heel and removed, the hardened flesh surface of the leather providing a substantial bearing surface for the removing tool. Moreover, during wear, such lifts exhibit substantially no fraying at the treated portions thereof.

Another aspect of this invention involves a process of impregnating leather from the flesh side with sulphur in the molten condition. This may be accomplished by floating the leather, in ordinary "air-dry" condition, on a bath of molten sulphur, or by supporting said leather at a predetermined depth of immersion therein, at a temperature and for a time sufficient to accomplish the desired impregnation. Generally speaking, the temperature of the molten sulphur is maintained as low as possible and relatively close to the melting point in order that the leather may not be injured. The time of immersion is regulated by the degree of impregnation desired, the time being proportional to the depth of penetration of the molten sulphur into the leather, and being sufficiently short as not to destroy the fibrous structure and the identity of the leather.

In another aspect, this invention relates to leather articles the entire exterior surfaces of which, including the grain surfaces, are impregnated to a predetermined degree with molten sulphur. Heel lifts of this character may be prepared. Another important example of this type of article is found in leather gaskets such as employed in fire hydrants. Leather fire hydrant gaskets contemplated by this invention possess considerably longer life than the gaskets hitherto used, due in part to the fact that the gaskets of our invention exhibit considerably greater resistance to the detanning action of the water to which they are exposed. Furthermore, valve sticking is greatly reduced due to a lessened corrosive effect upon the metallic valve seats with which the gaskets cooperate. Moreover, the gaskets of this invention exhibit generally better wearing properties under the difficult conditions to which they are subjected.

This invention further contemplates a method of preparing articles impregnated with molten sulphur throughout their exterior surfaces, such as fire hydrant gaskets, which method involves completely immersing such articles in molten sulphur at a temperature and for a time sufficient to accomplish the desired impregnation.

In the drawing,

Fig. 1 is a diagrammatic vertical sectional view of impregnating apparatus illustrating the impregnation of the flesh side and adjacent portions

of the leather by floating the leather on a bath of molten sulphur;

Fig. 2 is a diagrammatic vertical sectional view of impregnating apparatus illustrating the impregnation of leather from the flesh side by supporting the leather a predetermined degree below the surface of molten sulphur;

Fig. 3 is a perspective view, partially broken away, of a leather heel lift impregnated with molten sulphur from the flesh side, the impregnation extending toward, but not reaching, the grain side of the leather lift;

Fig. 4 is an elevation, partly broken away, of impregnating apparatus illustrating the impregnation of a leather fire hydrant gasket throughout its exterior surface; and

Fig. 5 is a perspective view of a leather fire hydrant gasket treated in accordance with this invention.

With respect to the impregnation of leather on its flesh side the invention may be carried out by floating the leather upon molten sulphur. Thus, by way of specific example and referring to Fig. 1, a bath of molten sulphur 2 in a shallow tray 4 was provided and the sulphur maintained at a temperature of 120 to 130° C. A leather heel lift 6 of ordinary vegetable-tanned sole stock and containing the ordinary amount of moisture of leather which has been exposed to the atmosphere, namely, "air-dry" leather, and having a thickness of about 9/48 of an inch, was floated on the molten sulphur 2 with the flesh side 8 of the lift downward. Care was taken in disposing the leather lift upon the molten sulphur to prevent contact of the molten sulphur with the upper or grain side 10 of the lift. The relative densities of the leather 6 and the sulphur 2 were such that the lift 6 was immersed to the extent of about three-fourths of its thickness. The leather lift 6 was allowed to remain in contact with the sulphur 2 for about 3 minutes during which period bubbles of air and moisture appeared in the sulphur 2 in the vicinity of the lift 6. The lift 6 was then removed from the sulphur bath in such a way as to prevent contact of the molten sulphur with the grain side 10 of the leather. After removal of the lift 6 from the molten sulphur bath 2, a portion of the excess sulphur on the edges 12 and flesh side 8 was wiped off by means of a cloth. Remaining traces of sulphur appearing on the surfaces 8 and 12 of the leather were caused to disappear into the substance of the leather by directing a blast of hot air at a temperature of about 140° C. at the surfaces 8 and 12 for about a minute. By this procedure, the sulphur remaining on the surfaces of the leather was melted and driven into the substance thereof, leaving no visible evidence on the surfaces of the presence of sulphur.

The heel lift 6 was impregnated as indicated at 14 with sulphur to about one-fourth of its thickness and from the flesh side 8. Penetration to a like extent had taken place from the edge surfaces 12. The impregnated portion 14 was relatively hard and stiff and free from any tendency to fray. The grain side 10 of the lift was in its original condition. The edges 12 of the leather lift 6 were found to receive leather finishes and polishes in a very satisfactory manner and to give results equal to, or even better than, ordinary leather in similar conditions. Moreover, the treated lift 6 was found to exhibit superior properties when used in association with a detachable heel construction, such as shown in the Gentile and Maccarone Patent No. 1,844,248. Thus, the metal prongs of a post of a detachable heel construction, such as shown in the patent above mentioned, were readily incorporated into the substance of the lift 6 from the flesh side thereof to form a secure mechanical attachment. Moreover, upon application to a shoe heel as part of such a detachable heel construction, lifts treated in the manner of this invention exhibited substantially no fraying in those portions thereof which had been impregnated with the sulphur. Furthermore, the flesh side 8 retained its hardness and firmness throughout the life of the lift, thereby providing a firm bearing surface for removal of the lift when worn. It has further been found that leather lifts treated in the manner above described resist the detanning action of water to a far greater extent than leather not so treated.

The use in a detachable heel construction of a leather lift prepared in accordance with this invention is disclosed and claimed in our copending application, Serial No. 158,018, filed August 9, 1937 (now Patent No. 2,189,812, granted February 13, 1940).

In Fig. 2 we have illustrated another mode of carrying out the impregnation of leather with sulphur from one side, especially the flesh side, only. This method is perhaps more suitable than the method indicated in Fig. 1 for the selective impregnation with sulphur of leather articles of relatively large size, although entirely applicable to small articles, such as heel lifts. Thus, in Fig. 2, the tray 16 contains a removable holder 18 with spaced horizontal supporting surfaces 20 arranged to carry leather stock 22, which may be "air-dry", immersed to a predetermined degree in the molten sulphur 24. The leather stock 22 is supported with the grain side 26 thereof above the surface of the sulphur 24 and with the flesh side 28 down and immersed in the sulphur. The spaced supporting surfaces 20 permit substantially complete contact of the sulphur with the lower or flesh side of the leather. In carrying out the impregnation, the leather 22 may be disposed on the surfaces 20 and removed therefrom while the holder 18 remains in the molten sulphur bath, or the holder 18 may be removed from the bath, the pieces of leather to be treated placed thereon, the holder 18 disposed in the tray 16 for the desired period of impregnation, and the holder subsequently removed therefrom. Other suitable arrangements may, of course, be provided for maintaining the leather at a predetermined depth of immersion in the sulphur bath.

In the case of either of the modes of impregnation illustrated in Figs. 1 and 2, a piece of leather stock of suitable size may be impregnated and subsequently smaller articles, such as heel lifts, may be died out or cut out of such larger pieces.

In carrying out the impregnation or "case hardening" of leather by means of the present invention, the leather, which may be of vegetable, chrome, or other tannage, may contain moisture to the extent of leather exposed to the atmosphere and in ordinary so-called "air-dry" condition. The temperature of the molten sulphur bath may be varied through a reasonable wide range although the temperature preferably remains below 150° C., in order to prevent destruction of the fibrous structure of the leather, and possible explosive evaporation of the moisture contained in the leather. The bath may be

maintained at a desired temperature in any suitable manner. The time of immersion will depend upon the depth of penetration or impregnation desired and upon the temperature of the molten sulphur. Generally speaking, the higher the temperature of the sulphur bath the shorter will be the time of immersion. We have found that suitable periods of immersion will range from 30 seconds in the case of sulphur baths having a temperature close to 150° C. to 20 minutes in the case of sulphur at temperatures close to the melting point. Between these extremes, by way of example, an immersion time of 5 minutes was found suitable in the case of a molten sulphur bath at a temperature of 125° C. The time of immersion and temperature of the sulphur bath is dependent upon the nature of a particular leather to be treated and in part upon the moisture content thereof. Too long a period of immersion is to be avoided in order to prevent attack on the substance of the leather by the molten sulphur and the destruction of the fibrous nature of the leather thereby.

By varying the depth of immersion of the leather in the sulphur bath, the characteristics of the impregnation may be varied. Thus if a piece of leather, such as a top lift of leather similar to sole stock is immersed in a sulphur bath, flesh side down, to an extent that only the grain surface remains out of the bath, the impregnation of the sulphur will take place simultaneously from the edges of the lift as well as from the bottom. After a relatively short period of immersion, therefore, the result will be substantially a case hardening effect on the edges and flesh side of the leather. Upon longer immersion the sulphur tends to penetrate from the flesh side further up through the leather, aided by capillary action, and the sulphur tends to penetrate to a level at least equal to that of the sulphur in the bath. If the leather is immersed flesh side down in the sulphur to only a slight degree of immersion, the penetration of the sulphur takes place substantially entirely on the flesh side.

Where excess sulphur remains on surfaces of leather articles which have been immersed in the molten sulphur bath, such excess may be removed in any suitable manner, for example, by wiping, scraping, abrading or by melting the sulphur and driving it into the leather by means of a hot air blast at a temperature above the melting point of sulphur.

In Figs. 4 and 5 we have illustrated the application of this invention to a case wherein it is desired to impregnate any leather article over its entire surface area. Specifically, we have illustrated a fire hydrant gasket **30** consisting of a plurality of plies **32** of leather which are joined together by a suitable adhesive, such as pyroxylin. In order to accomplish the impregnation of the gasket **30** throughout its surface extent and to provide a "case hardening" effect, the gasket **30** is disposed in the molten sulphur bath **34** contained in the tray **36**. The gasket **30**, which normally would tend to float in the molten sulphur, may be held under the surface thereof by any suitable means, such as a weight **38**. Preferably the supporting means **40** are provided upon which the gasket **30** may rest above the bottom of the tray **36**, said supporting means **40**, as well as the weight **38**, being so arranged as to permit the molten sulphur to contact with the surface of the gasket **30** throughout its extent. With the molten sulphur at a temperature of 130° C. a suitable impregnation may be accomplished by permitting the gasket **30** to remain in the molten sulphur **34** for a period of about 6 minutes. The temperatures and times of immersion of the gasket in the sulphur may be varied within limits such as previously suggested. After removal of the gasket **30** from the molten sulphur bath any excess sulphur remaining on the surface of the gasket may be removed by wiping, scraping, abrasion or by means of a hot air blast at a temperature above the melting point of sulphur, for example 140° C.

A gasket treated in the manner described above has unique properties when employed in a fire hydrant in that the presence of the sulphur imparts to the gasket the property of resisting the detanning and deteriorating effect of water to a far greater degree than ordinary untreated leather. Such increased resistance to detanning and a consequent retention of tannic acid in the leather diminishes the corrosive effect on the metal valve seat with which the gasket contacts and consequently the occurrence of valve sticking is greately minimized, if not substantially eliminated.

The aspect of this invention pertaining to the impregnation of a leather article throughout its exterior surface may also be practiced with respect to a heel lift, in which case the lift is completely immersed in a sulphur bath.

When practicing this invention in any of its aspects and particularly when a somewhat greater flexibility in the product is desired, a plasticizer may be incorporated in the molten sulphur bath. While various materials might be employed for this purpose we have found that olefine polysulphide (which may be obtained under the commercial name of "Thiokol") is advantageous for this purpose because of its compatibility with sulphur. While various percentages may be employed we have found that the incorporation of about 2% of Thiokol in the sulphur imparts to the treated leather product a satisfactory degree of flexibility while retaining the desired effects of the molten sulphur thereon. Other plasticizers, such as rubber, may be employed in place of "Thiokol."

Having described our invention, what we claim as new and desire to secure by Letters Patent of the United States is:

The method of impregnating leather with sulphur which comprises immersing said leather in a bath of molten sulphur, and subsequently directing on the previously immersed portions of the leather a blast of air at a temperature above the melting point of sulphur.

JOHN H. McGILL.
WALTER H. WEDGER.