

## UNITED STATES PATENT OFFICE

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IMPREGNATION OF LEATHER AND  
PRODUCTS THEREOF

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My invention pertains to the preservation and treatment of leather by impregnating leather with a polymer obtained by the polymerization of a mixture of both normal and iso-butene, and articles of manufacture and leather impregnating compositions containing such polymers.

All natural fat and oil must be removed from hide prior to tanning to permit penetration of the tanning liquors. Dried, tanned leather is stiff because the natural lubricant has been removed and the fibre bundles fail to slide against and between each other. Leather in this condition deteriorates rapidly if the leather is repeatedly bent or flexed because the friction of the individual fibres causes internal wear. A lubricant and preservative must be added to leather before it is used, to replace the natural fat and oil removed prior to tanning, and to prevent deterioration caused by internal wear.

Various compositions have been used for this purpose, among which are neat's-foot oil, fish oil and castor oil. The best oils soften and preserve leather, and do not become rancid or greasy and discolor the leather.

The use of the polymer described and claimed herein has been found to have numerous advantages. When properly prepared it is water white and hence does not discolor leather. It is highly stable and, therefore, does not become rancid. By reason of the fact that it does not hydrolyze and liberate stearic acid in the manner of ordinary fats and oils, it does not produce the objectionable bloom characteristics of many leather preservatives. It has additional advantage in that it can readily be rendered odorless and tasteless by hydrogenation. Even if such hydrogenation step is omitted the odor and taste of the polymer is slight. A most important feature of the polymer is that it is normally liquid, even at temperatures as low as  $-100^{\circ}\text{F.}$ , and, thus, may be used directly as a preservative without the use of any solvent or emulsifying agent. In this it has great advantage over solids, such as iso-butene polymers, used as leather preservatives. The polymer is soluble in mineral oils and in most other substances with which leather is impregnated.

The polymer described and claimed herein as a leather preservative is derived from the polymerization of a mixture of normal and iso-butene, the ratio of normal butene to iso-butene being substantial, under circumstances such that both the normal and the iso-butenes are polymerized. Appropriate sources of such olefines are gases

obtained from thermal cracking of petroleum, crude oil, distillates or residuums.

Sulfur compounds in the charging stock such as hydrogen sulfides and low boiling mercaptans are preferably removed prior to polymerization. These may be removed by use of an aqueous alkaline hydroxide such as sodium hydroxide to form water soluble products, or by use of sodium plumbite and the conventional doctor treatment.

The sulfur free olefinic material is dried, cooled and then polymerized in either gaseous or liquid phase, the latter being preferred, with the aid of a polymerization catalyst, usually anhydrous aluminum chloride. The reaction temperature is preferably at approximately atmospheric. However, lower and higher temperatures, below  $120^{\circ}\text{F.}$ , have been found satisfactory. If gaseous phase polymerization is used, the gas may be bubbled through a suspension of anhydrous aluminum chloride in petroleum ether.

The removal of aluminum chloride sludge may be accomplished by settlement, filtration through a rock filter, followed by clay treatment.

The polymers may then be separated from the accompanying unpolymerized lower boiling point hydrocarbons, such as butane, by any ordinary vaporization process, and the polymers themselves may be segregated into various cuts or fractions according to viscosity or volatility desired by ordinary processes of distillation with fractionation. The unpolymerized normal and iso-butene, together with accompanying lower boiling point hydrocarbons, may be recycled for the polymerization of the unpolymerized normal and iso-butene.

The entire polymer product may be subjected to a saturating, non-destructive hydrogenation at super-atmospheric temperature and pressure in the presence of a hydrogenating catalyst such as finely divided catalytic nickel.

The percentage of polymerized iso-butene in the final product of the polymerization step has an important effect on the viscosity of the butene-iso-butene polymer. The higher the percentage of iso-butene polymers in the finished product the higher the viscosity of the finished product. Table 1 below illustrates such effect:

Table 1

|                                                     |     |     |     |     |
|-----------------------------------------------------|-----|-----|-----|-----|
| Percent of iso-butene polymers.....                 | 37  | 47  | 52  | 65  |
| Viscosity at $210^{\circ}\text{F.}$ (S. S. U.)..... | 100 | 195 | 260 | 465 |

The ratio of iso-butene in the butene-iso-butene polymer can be controlled in various ways, such as by controlling percentage of iso-butene

in the charging stock, and by control of polymerization temperature, since normal butene polymerizes scarcely at all below 0° F., while iso-butene will polymerize quite readily at 0° F. and below. Thus by keeping the polymerization temperature within the desired proximity to 0° F. the percentages of normal and iso-butene polymerized can be controlled.

The percentage of normal to iso-butene present in the charging stock does not seem to be important. The important factor is the percentages of such constituents present which are in fact polymerized. If the temperature rises above 0° F. for any appreciable time the normal butenes polymerize rapidly enough so that their proportion of the finished mixture is substantial. Table 2 below is illustrative of results obtained by the polymerization of a mixture of normal and iso-butene in a continuous system:

Table 2

|                                                                  | Run  |      |      |      |
|------------------------------------------------------------------|------|------|------|------|
|                                                                  | 1    | 2    | 3    | 4    |
| Percent of normal butene in charging stock                       | 28.1 | 27.2 | 27.6 | 29.1 |
| Percent iso-butene in charging stock                             | 13.5 | 12.6 | 13.7 | 12.8 |
| Percent normal butene in recycle stock                           | 15.5 | 17.7 | 18.0 | 16.9 |
| Percent iso-butene in recycle stock                              | 3.9  | 4.0  | 4.7  | 4.0  |
| Percent polymers from normal butene                              | 48.0 | 49.2 | 49.2 | 56.0 |
| Percent polymers from iso-butene                                 | 40.5 | 41.5 | 41.3 | 39.0 |
| Volumes of liquid charging stock per volume of catalyst per hour | 0.8  | 0.7  | 0.6  | 1.4  |
| Recycle ratio, volume of recycle stock per volume of fresh stock | 2.5  | 2.6  | 2.7  | 2.7  |
| Temperature, ° F., in                                            | -33  | -40  | -35  | -24  |
| Temperature, ° F., out                                           | +57  | +42  | +44  | +25  |
| Average temperature of polymerization, ° F.                      | 12   | 1    | 4    | 0    |
| Viscosity at 210° F. (S. S. U.)                                  | 76   | 213  | 135  | 225  |
| Percent conversion, normal butene                                | 61   | 54   | 54   | 60   |
| Percent conversion, iso-butene                                   | 100  | 99   | 92   | 95   |

In order to produce a viscous, liquid polymer it is necessary that the charging stock contain both normal and iso-butene and that both be polymerized in substantial portions. The polymer described herein must be distinguished from the plastic solid polymer obtained by the polymerization of iso-butene alone. If iso-butene and normal butene are separately polymerized and then mixed, such mixture will not produce the polymer described herein as a leather oil.

The molecular weight of the polymer fraction used for impregnation of leather will vary with the type and function of the leather impregnated. It has been found that for many leather treating purposes a molecular weight less than 600 is highly desirable. In general, under the method described above, cuts are obtainable from the polymer varying from 200 to 780 in molecular weight.

Among the fractions from such polymerized mixtures of normal and iso-butene used successfully for treating leather, is a fraction having the following characteristics:

|                                |      |
|--------------------------------|------|
| Gravity, A. P. I.              | 31.8 |
| Flash                          | 350  |
| Viscosity, S. S. U. at 100° F. | 4782 |
| Viscosity, S. S. U. at 210° F. | 213  |
| Color, A. S. T. M.             | 1.5  |

The method of impregnating leather as described and claimed herein has been found valuable not only for the more common uses of leather, but has been found especially valuable for the impregnation of leather gas meter diaphragms. Such diaphragms must, for accuracy, remain flexible for long periods under conditions which tend rapidly to harden leather. Ordinary leather preservatives of sufficiently high viscosity are not satisfactory for such purpose.

The description given above is merely illustrative. Numerous variations of manufacture and use may be made within the scope of the appended claims.

I claim:

1. The method of treating leather, which comprises impregnating the leather with a polymer obtained by polymerization of a mixture of both normal and iso-butene.

2. The method according to claim 1 in which the polymer is normally liquid.

3. The method according to claim 1 in which the polymer is of a molecular weight from 200 to 780.

4. The method of treating leather which comprises impregnating the leather with a normally liquid polymer of a mixture of both normal and iso-butene, said polymer having a molecular weight less than 780 and more than 200.

5. An article of manufacture comprising a leather, having incorporated therein a normally liquid polymer of a mixture of both normal and iso-butene.

6. An article of manufacture comprising a leather having incorporated therein a normally liquid polymer of a mixture of both normal and iso-butene, said polymer having a molecular weight less than 780 and more than 200.

7. A leather impregnating composition having the quality of keeping leather soft and flexible without being sticky and being substantially non-volatile and capable of being used as a leather dressing without admixture with any other substance comprising a normally liquid polymer of a mixture of both normal and iso-butene and having a molecular weight less than 780 and more than 200.

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