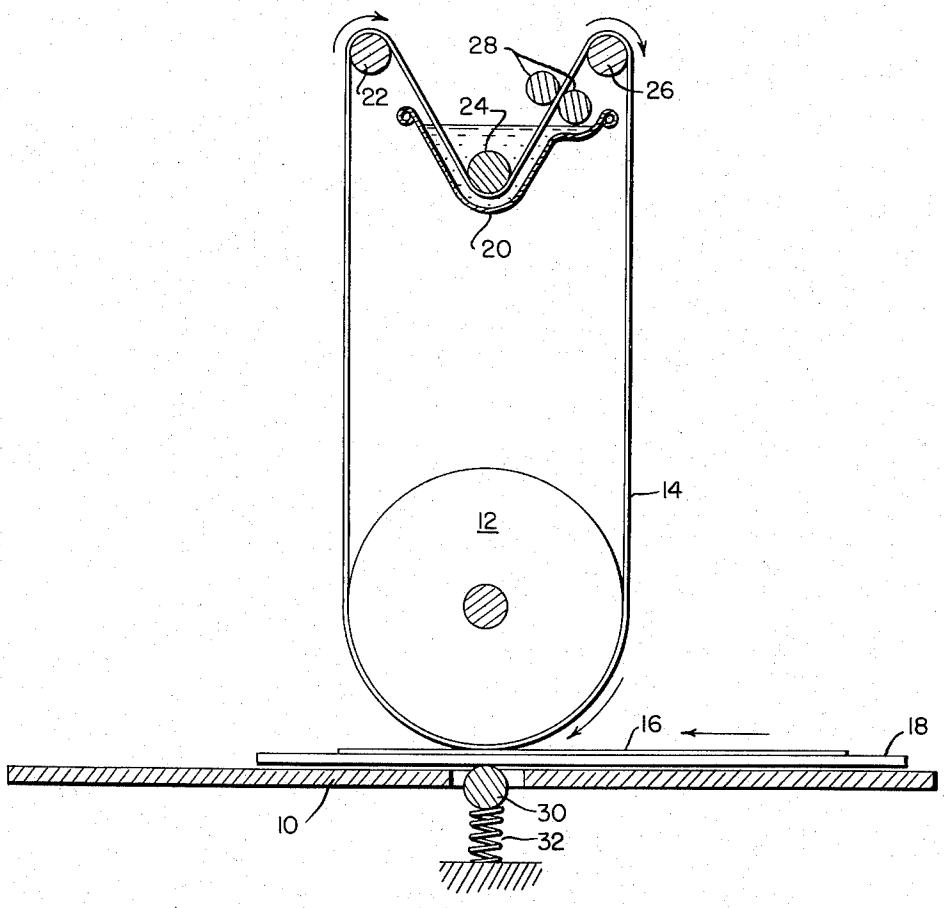
Jan. 13, 1959 A. E. USHAKOFF 2,868,614

FATTING OF SKINS

Filed April 28, 1954



INVENTOR.
ALEXIS E. USHAKOFF

BY
Kenway, Jenney, Witter & Hildreth

ATTORNEYS

United States Patent Office 2,868,614
Patented Jan. 13, 1959

2,868,614

FATTING OF SKINS

Alexis E. Ushakoff, Beverly, Mass., assignor, by mesne assignments, to Nathan W. Levin, New York, N. Y., Alexis E. Ushakoff, Somerville, Mass., and J. B. Hatton, Grand Haven, Mich., as trustees

Application April 28, 1954, Serial No. 426,151

20 Claims. (Cl. 8—94.18)

The present invention is directed to the fatting of skins or leather, particularly leather produced by solvent tannage processes in which the water of a normally wet hide or skin is extracted and replaced with a water-miscible organic solvent, and at least the final tanning steps are carried out under non-aqueous conditions.

The fatting of skins or leather consists in general in the application of any of numerous oily, greasy, or fatty substances to the wet skin, primarily to prevent the skin fibers from coalescing during drying, and also to lubricate the fibers and to enhance the water repellency of the leather. According to conventional tanning practice, fatting is carried out by applying an oil, grease or fat to the water-wet skin after the skin has been treated with the tanning agent and prior to drying, ordinarily, by drumming the skin in a water emulsion of the fatting agent or in a liquid fat, using outside heat if necessary, or by repeatedly swathing the skin with the fat. In such treatments the fatting agent becomes distributed through the skin primarily by diffusion, and it is ordinarily necessary to maintain the skin in the presence of excess fat for a sufficient time for the fat to diffuse through the skin.

Solvent tannage processes have numerous advantages over tannages carried out in the presence of water, an important one being that by replacing the water with an organic solvent, careful control over the drying of the skin is not required. Whereas, a water-wet skin should, for best results, be dried slowly with frequent mechanical manipulation, and in the presence of fatting agents to maintain the desired softness and pliability, a skin in which the water is replaced with an organic solvent may be dried rapidly and without a fatting agent, and will still maintain a high degree of its inherent softness and pliability. It is nevertheless, desirable to add fatting agents to leather produced by solvent tannage to lubricate the fibers, increase the water-repellency, enhance the softness and pliability, and to permit the skin to be re-wet with water and dried without becoming brittle and horny. Conveniently, the fatting of a solvent tanned skin is carried out by treating the skin after it has been treated with the tanning agent, with an organic solvent solution of the fatting agent, for instance, by drumming the skin in the solution or by forcing the solution through the skin under a fluid-pressure differential.

The present invention provides a rapid and economical process of applying fatting agents to a skin, and in its preferred embodiments results in the skin having a far greater tear resistance and tensile strength than is imparted by other fat liquoring processes. In the process of this invention, the fatting agent is first applied to the skin in the required amount, and then caused by subsequent processing steps to become distributed through the skin. It is thus unnecessary to maintain the skin in the presence of the fatting agent for the time required for impregnation, or to treat the skin with an excess of the fatting agent.

Solvent tannage processes in general, are similar to conventional processes carried out in the presence of water in the sense that a tanning agent is incorporated in the skin and chemically fixed therein as by neutralization, and the skin is then dried. These steps may be performed entirely in the presence of the organic solvent, or the process may be carried out in the presence of water in its initial steps, following which the water is extracted and replaced with the solvent and then dried from the solvent-wet condition. Thus, a water-wet untanned skin may be first treated with the solvent, and the entire tanning process carried out under non-aqueous conditions by employing tanning agents dissolved in organic solvents, as disclosed in copending application, Ser. No. 233,924 filed June 27, 1951, now Patent No. 2,702,229 or the initial water-wet skin may first be treated with an aqueous solution of a tanning agent, then treated with the extracting solvent, and further processed under non-aqueous conditions, as disclosed in copending application, Ser. No. 330,632 filed January 12, 1953, now Patent No. 2,767,043.

In carrying out the present invention, the skin will ordinarily have been treated with tanning agents and will have been substantially dehydrated, as by contacting the skin with the solvent until the water is extracted and replaced by the solvent, and will be wet with the solvent, preferably, one in which the fatting agent is soluble. In general, the invention consists in applying a surface coating of the fatting agent to the skin and thereafter drying the skin preferably by the application of external heat to one or both of its surfaces to cause the fatting agent to penetrate rapidly into the interior of the skin and become distributed throughout.

It has been found that applying heat to accelerate the drying causes a rapid and complete distribution of the fatting agent throughout the skin. It has also been observed that the fatting agent is apparently drawn into the skin as the solvent escapes during drying, and further that the fatting agent tends to follow the solvent and concentrate to a certain extent in the region where the solvent is removed. Thus, if a fatting agent is applied to one surface and the skin is dried from the opposite surface, the fatting agent will be found to have a relatively higher concentration at the surface opposite from the one to which it was applied. This characteristic it will be seen affords an important degree of control over the distribution of the fatting agent.

Best results have been obtained if the skin is solvated with the organic solvent when the fatting agent is applied. The solvated condition exists from the time the water is extracted and replaced with the organic solvent until the skin is dried of the solvent, and is believed to result from the replacement by the solvent of not only the water in the fiber interstices, but also of the bound water which apparently hydrates the fiber substance. If a skin is dried and then rewet with a solvent, the solvent apparently fills only the fiber interstices without solvation of the fiber substance, for much less solvent is present in the skin than when the water is extracted and replaced by solvent. Although this behavior is not fully understood it is hypothetized that desolvation of the fiber substance is irreversible.

Whether a skin is solvated, or merely wet with solvent without being solvated, may be readily determined by first weighing a sample of the skin, then drying it, rewetting it with the solvent and reweighing it. If the skin is solvated, the initial weight will be in excess of its weight after drying and rewetting, whereas, if the skin is merely wet with solvent, the two wet weights will be substantially the same.

It is also to be noted that a skin once solvated as by

the extraction of water with solvent will remain solvated until dried, and may be tanned in the solvated condition for instance, by immersing the solvated skin in an organic solvent solution of a tanning agent as disclosed in copending application, Ser. No.233,924 filed June 27, 1951, now Patent No. 2,702,229, or it may be treated with a tanning agent under aqueous conditions, and then solvent dehydrated to solvate it, as disclosed in my copending application, Ser. No. 330,632 filed January 12, 1953, now Patent No. 2,767,043.

Although best results are had if the skin is solvated with the organic solvent, the application of the fatting agent to a solvent-wet skin, for instance, one dried then rewet with solvent, also produces improved results, notably in the control afforded over the distribution of the fatting agent.

Solvents which may be used in practicing this invention generally include organic liquids which are water-miscible and non-injurious to the skin, and in which the fatting agent is soluble, for instance, alcohols such as methanol, ethanol, and isopropanol; ketones such as acetone and methyl ethyl ketone, and similar organic liquids.

Fatting agents which may be used include those commonly used in conventional tanning practice such as neats foot oil, cod liver oil, mineral oils, and vegetable oils such as caster oil, peanut oil or olive oil. Particularly preferred, however, as fatting agents are the fatty acids, such as lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid, to name a few of the more common ones. Fatty acids have, of course, been used in preparations for treating leather, but without particular benefit accredited to them. If applied, however, to a solvated skin they result in a marked increase in its tensile strength. In this connection it has been found that the tensile strength is increased with increasing amounts of fatty acid up to about 3% on the weight of dry skin. Above 3%, additional fatty acid has little effect on the tensile strength, but may be desired for other reasons, for instance, to impart greater water repellency, or to increase further, the pliability or softness of the leather.

The fatting agent is preferably applied to the skin as a liquid, and may accordingly be a normally liquid material, such as the various oils and oleic acid, or may be a solution of the fatting agent, for instance, a solution of a normally solid fatty acid in acetone, or other solvent. The application of the fatting agent as a surface coating to the skin may be done by hand, as by painting it on the skin, or it may utilize any of a number of mechanical applicators such as a printing drum to which is applied the fatting agent as a surface coating.

After the fatting agent has been applied in the desired amount, the skin is dried of the organic solvent to cause the fatting agent to become distributed throughout. Drying is preferably accelerated by the application of external heat, conveniently by contacting the skin at one or both of its sides with surfaces heated above the boiling point of the solvent. Suitable apparatus for this purpose is disclosed in detail in copending application, Ser. No. 393,329 filed November 20, 1953, now Patent No. 2,803,889.

A preferred embodiment of this invention selected for purposes of illustration is described in detail below. The tanning process preliminary to the application of the fatting agent is one giving good results and is presented as typical of a solvent tannage process. The particular solvent, acetone, and fatting agent, oleic acid, are similarly presented as representative of these types of materials.

The drawing is a cross-sectional view of suitable apparatus for applying a surface coating of a liquid fatting agent to a skin.

A wet bated cowhide is drummed until pickled in twice its weight of an aqueous solution containing 4% by weight of salt (NaCl) and having a pH of 2.0 imparted by the addition of sulfuric acid. After the skin is thoroughly pickled, 10%, based on the weight of the skin, of Tanolin T (a typical medium basic soluble chromium sulfate tanning agent), sold by Diamond Alkali Corp., Cleveland, Ohio, and having the following analysis:

	Percent
Cr_2O_3	23.5
Hydrolyzable SO_3	20.8
Al_2O_3	1.6
Na_2SO_4	51.8
Basicity	42–44

is dissolved in hot water to a concentration of about 20% by weight and added to the drum, and the skin is tumbled until the tanning solution has fully penetrated the skin. During this time, the tanning bath is heated to about 140° F., always maintaining the bath temperature below the shrinkage temperature of the skin by at least about 20 Fahrenheit degrees, as the shrinkage temperature of the skin rises to about 160° F. Sodium bicarbonate is then added slowly to the drum until the pH of the solution has reached 3.8–4.0 during which time the bath is heated to about 160° F. The skin is then removed from the drum, washed in fresh water to remove excess dissolved salts, and solvent dehydrated with acetone by supporting the skin on a porous surface and forcing the acetone through it under a fluid pressure differential, with apparatus and as described more fully in my copending application, Ser. No. 393,377 filed November 20, 1953, now abandoned. During dehydration in this manner, the skin is supported on a porous tray, and further processing in accordance with this preferred embodiment of the invention is carried out with the skin supported on the tray. A suitable tray construction is described in detail in the above identified copending application, Ser. No. 393,377 filed November 20, 1953, now abandoned.

At this stage the skin contains the tanning agent and is solvated and wet with the organic solvent, and is thus in condition for fatting in accordance with this invention. The fatting process is carried out by applying a surface coating of oleic acid to the solvated skin, by contacting the skin with an applicator surface supplied with the oleic acid. Suitable apparatus is shown in cross-section in the drawing, and consists in general of a bed member **10** and an overlying parallel cylinder **12** around the lower side of which passes a bibulous belt **14** carrying the fatting agent. The skin **16**, supported on the porous tray **18**, is passed in rolling contact with the belt **14**, by feeding the tray and skin along the bed **10** beneath the cylinder **12**, whereby a surface coating of the fatting agent is deposited by the belt on the surface of the skin.

The belt **14** conveniently formed of flannel or other absorbent fabric, feeds continuously with rotation of the cylinder **12** through a trough **20** mounted over the cylinder **12** and in which is contained the fatting agent. Control over the belt **14** is provided by a receiving roller **22** guiding the section of the belt travelling from the cylinder into the trough, a dunking roller **24** mounted in the trough and guiding the belt through the fatting agent, and a let-off roller **26** guiding the section of the belt travelling from the trough to the cylinder **12**.

To provide control over the amount of fatting agent carried by the belt **14**, a pair of squeeze rollers **28** through which the belt feeds after emerging from the trough **20**, are mounted over the trough between the dunking roller **24** and the let-off roller **26**, in mechanism permitting adjustment of the pressure between them. By varying this pressure, the amount of fatting agent carried by the belt is readily controlled.

To assure contact between the belt **14** and skin **16**, as the skin is fed beneath the cylinder **12**, a bed roller **30** is yieldingly mounted, as in journals supported by springs **32**, beneath the cylinder **12** to urge the tray **18** and skin **16** upward against the belt.

The cylinder **12** and rollers **22**, **24**, **26**, **28** and **30** may be driven by conventional mechanism, to carry the skin and tray between the cylinder **12** and bed roller **30** by

frictional engagement, or they may be mounted to rotate freely to be driven by the frictional force of the skin and tray as it is forced between the cylinder **12** and bed roller **30**.

The amount of fatting agent applied to the skin in this manner may vary considerably according to the characteristics desired in the final product. Since fatting agents are not required to prevent coalescence of the fibers when drying a solvent wet skin, less fatting agent than is commonly applied in conventional aqueous processes may be entirely satisfactory. When fatty acids are employed as the fatting agent, generally at least 3% on the weight of the dry skin is preferred to attain maximum strength, but frequently more or less may be desired.

The fatting agent is preferably a liquid, either in itself or by virtue of being in solution, and the amount applied may readily be controlled by varying the pressure exerted on the belt **14** by the squeeze rollers **28**, by varying the concentration of the fatting agent, or by applying repeated surface coatings. In any case, however, the fatting agent in the desired amount is applied to the skin, and is thereafter caused to become distributed throughout by the subsequent drying step.

The skin with the surface coating of the fatting agent is finally dried of the solvent, conveniently by bringing the skin, while supported on the tray between a pair of surfaces heated to a temperature above the boiling point of the solvent. Apparatus suitable for this purpose is described in detail in copending application, Ser. No. 393,329 filed November 20, 1953, now Patent No. 2,803,-889. This apparatus consists in general of a heated foraminous platen and an overlying steam inflated diaphragm. The skin and tray are placed between the platen and diaphragm and the diaphragm is then inflated with steam to contact the skin, thereby subjecting the skin to rapid heating from its top and bottom surfaces. The solvent vapors formed escape through the porous tray and foraminous platen, and may be collected in a manifold to which the openings in the platen lead and passed to a solvent recovery system. If desired the pressure in the manifold may be reduced to permit drying at a lower temperature.

The dry skin will be seen to be of high quality with the fatting agent distributed throughout its thickness. In the foregoing example, a fatty acid was applied to the skin while solvated, resulting in a remarkably high tear resistance and tensile strength. Although this particular effect is not realized when other ordinary fatting agents are used, nor when the fatty acid is applied to a skin merely wet with solvent but not solvated, the invention when practiced under such less preferred conditions nevertheless provides high quality leather at least equivalent to that prepared by prior art fatting processes, and in addition provides the advantages of rapid and economical application of the fatting agent.

The printing technique of applying the fatting agent, described above, is particularly advantageous when treating skins supported on a porous plate, in that the fatting agent is applied selectively to the skin, by virtue of its surface being elevated above the supporting surface of the plate, and not to the areas of the plate uncovered by the skin.

It is to be noted that insofar as this invention relates to the use of a fatty acid in fat liquoring solvated skins, the improved characteristics imparted by fatty acids are realized independently of the method by which applied. The fatty acid may accordingly be applied by treating a solvated skin with a solution of a fatty acid, as by drumming the skin in the solution, or by forcing the solution through the skin as disclosed in copending application, Ser. No. 330,632 filed January 12, 1953, now Patent No. 2,767,043, or by treating a solvated untanned skin with an organic solvent solution containing a tanning agent, preferably partially neutralized, and a fatty acid, as disclosed in copending application, Ser. No. 100,965 filed

June 23, 1949 now abandoned. In this connection it is to be noted that although ordinarily a fatty acid will be applied to a skin after it has been treated with a tanning agent, the presence of the tanning agent is not essential to the strengthening effect of the fatty acid. A solvated skin, free of any tanning agent, if similarly treated with a fatty acid, will have the enhanced tear resistance and tensile strength imparted by the fatty acid.

Having thus disclosed my invention and described in detail a preferred embodiment thereof, I claim and desire to secure by Letters Patent:

1. The method of fatting skins comprising supporting a skin wet with an inert volatile organic solvent on a porous supporting surface, applying a liquid surface coating of a leather fatting agent to the skin by contacting its unsupported surface with an applicator surface carrying the fatting agent and thereby depositing the fatting agent on the unsupported surface of the skin without depositing fatting agent on the supporting surface, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

2. The method of fatting skins, comprising supporting a skin wet with an inert volatile organic solvent on a porous supporting surface, applying a liquid surface coating of a leather fatting agent to the skin by contacting its unsupported surface with an applicator surface carrying the fatting agent and thereby depositing the fatting agent on the unsupported surface of the skin without depositing fatting agent on the supporting surface, and drying the skin by heating the skin to remove the solvent and to cause said agent to be distributed through the skin.

3. The method of treating skins comprising contacting a water-wet skin with water-miscible volatile inert organic solvent until the water is extracted and replaced by said solvent, maintaining the skin wet with solvent, applying fatty acid which is a leather fatting agent to the skin, and finally drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

4. The method of fatting skins comprising contacting a water-wet skin with a water-miscible organic solvent until the water is extracted and replaced by said solvent, applying to the surface of said skin a predetermined amount of a fatty acid feather fatting agent as a surface-coating on said skin while said skin is wet with solvent, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

5. The method of fatting skins comprising applying a liquid coating comprising a leather fatting agent to a surface of a skin wet with a volatile inert organic solvent in which said agent is soluble, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

6. The method of fatting skins comprising applying a liquid coating comprising a leather fatting agent to a surface of a skin in which bound water has been replaced by contacting said skin with an inert volatile organic solvent in which said agent is soluble until the solvent is present in the skin in place of the bound water, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

7. The method of fatting skins comprising applying a liquid coating containing a fatty acid which is a leather fatting agent to the surface of a skin in which bound water has been replaced by contacting said skin with an inert volatile organic solvent in which said fatty acid is soluble until the solvent is present in the skin in place of the bound water, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

8. The method of fatting skins comprising applying a liquid surface coating containing the desired amount of a leather fatting agent to a surface of a skin wet with a volatile inert organic solvent in which said agent is

soluble, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

9. The method of fatting skins comprising applying a liquid surface coating containing the desired amount of a leather fatting agent to a surface of a skin in which bound water has been replaced by contacting said skin with an inert volatile organic solvent in which said agent is soluble until the solvent is present in the skin in place of the bound water, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

10. The method of fatting skins comprising applying a liquid surface coating containing the desired amount of a fatty acid which is a leather fatting agent to a surface of a skin in which bound water has been replaced by contacting said skin with an inert volatile organic solvent in which said fatty acid is soluble until the solvent is present in the skin in place of the bound water, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

11. The method of fatting skins comprising applying a liquid coating of a leather fatting agent to a surface of a skin wet with an inert volatile organic solvent in which said agent is soluble, and drying the skin by heating the skin to a temperature above the vaporization temperature of the solvent to remove the solvent and to cause said agent to be distributed through the skin.

12. The method defined by claim 11 wherein the skin is heated by contacting it with a surface heated to a temperature above the vaporization temperature of the solvent.

13. The method defined by claim 12 wherein the skin is pressed between a pair of heated surfaces.

14. The method of fatting skins comprising applying a liquid coating containing a fatty acid which is a leather fatting agent to the surface of a skin in which bound water has been replaced by contacting said skin with an inert volatile organic solvent in which the fatty acid is soluble until the solvent is present in the skin in place of the bound water, and drying the skin by heating the skin to a temperature above the vaporization temperature of the solvent to remove the solvent and to cause said agent to be distributed through the skin.

15. The method defined by claim 14 wherein the skin is heated by contacting it with a surface heated to a temperature above the vaporization temperature of the solvent.

16. The method defined by claim 15 wherein the skin is pressed between a pair of heated surfaces.

17. The method of fatting a skin comprising contacting a surface of a skin wet with an inert volatile organic solvent with an applicator surface having a liquid coating of a leather fatting agent thereon, thereby depositing a coating of said agent on the surface of the skin, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

18. The method of fatting a skin comprising passing a surface of a skin wet with an inert volatile organic solvent in rolling contact with cylindrical applicator surface having a liquid coating of leather fatting agent thereon, thereby depositing a coating of said agent on the surface of the skin, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

19. The method of fatting a skin comprising applying a fatty acid which is a leather fatting agent to a skin in which bound water has been replaced by contacting said skin with an inert volatile organic solvent in which said fatty acid is soluble until the solvent is present in the skin in place of the bound water, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

20. The method of treating skins comprising contacting a water wet skin with a water-miscible inert volatile organic solvent to extract and replace the water in the skin with said solvent, then applying a fatty acid which is a leather fatting agent to the skin while the skin is wet with solvent, and drying the skin to remove the solvent and to cause said agent to be distributed through the skin.

References Cited in the file of this patent

UNITED STATES PATENTS

707,752	Belledin	Aug. 26, 1902
1,193,927	Ruhe	Aug. 8, 1916
1,200,146	Spalteholz	Oct. 3, 1916
1,258,729	Winneur	Mar. 12, 1918
1,540,791	McDill	June 9, 1925
1,695,963	Koeniger	Dec. 18, 1928
2,086,792	Fabian et al.	July 13, 1937
2,176,434	Niedercorn	Oct. 17, 1939
2,661,543	Tyndall et al.	Dec. 8, 1953
2,702,229	Ushakoff	Feb. 15, 1955

FOREIGN PATENTS

312,697	Great Britain	May 31, 1929
243,091	Great Britain	Nov. 26, 1925

OTHER REFERENCES

Koppenhoeffer: J. I. S. L. T. C., July 1944, pp. 176–177.