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# UNITED STATES PATENT OFFICE

WILHELM PUNGS, OF LUDWIGSHAFEN-ON-THE-RHINE, AND KARL BEHRINGER, OF MANNHEIM, GERMANY, ASSIGNORS TO I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, OF FRANKFORT-ON-THE-MAIN, GERMANY, A CORPORATION OF GERMANY

## PRODUCTION OF PRODUCTS RESEMBLING NATURAL WAXES

No Drawing. Application filed April 5, 1929, Serial No. 352,902, and in Germany April 13, 1928.

The present invention relates to the production of products resembling natural waxes.

In certain other applications for patents one of the present inventors, either alone or in conjunction with others, has described processes for the production of valuable products from crude or de-resinified Montan wax. These processes generally deal with the purification of these waxes by bleaching operations performed by means of solutions of oxidizing agents. Thus for example Montan wax has been bleached by means of solutions of chromic acid in aqueous solution or in a solution of acetic acid or with a continuously regenerated solution by carrying out electrolytically the said bleaching operation; and numerous variations of these processes have been suggested by one of the present inventors for further improving the properties of the bleached Montan wax, for example by bleaching the wax and simultaneously saponifying the wax esters contained therein or by subjecting a bleached Montan wax to a distillation. Such processes are described and claimed for example in the applications Ser. No. 247,454, filed January 17, 1928, Ser. No. 254,604, filed February 15, 1928 and in the U. S. A. Patents Nos. 1,690,876, 1,737,975 and 1,698,450. In several of these applications and in the applications Ser. No. 330,612, filed January 5, 1929 and Ser. Nos. 352,903 and 352,904 filed April 5, 1929, the conversion of the acids contained in the bleached wax into amides, anhydrides, esters or salts or mixtures of these compounds and the condensation of the said acids with organic hydroxyl-bearing substances has been described and claimed by which processes the properties of the bleached Montan wax can be varied as desired. The aforesaid condensation of the acids contained in the bleached wax is favorably carried out by combining organic carboxylic acids, such as fatty or aromatic or hydroaromatic acids, or materials containing the same either in the free state or in the form of esters, with the said acids of the bleached wax by means of polyhydric alcohols or other hydroxy compounds thus forming a bridge between the said different acids. For the sake of brevity the Montan wax bleached by means of solutions of oxidizing agents will be referred to in the following and in the claims as bleached Montan wax and the products prepared from bleached Montan wax will be referred to as converted bleached Montan wax.

We have now found that new substances, resembling natural waxes in their physical properties, ranging between those of Japan and carnauba wax, can be obtained by treating the bleached Montan or the converted bleached Montan wax either alone or in conjunction with plastic or even liquid organic substances of high molecular weight, such as paraffin wax or paraffin oil, or substances of an oily, fatty, resinous or waxy character, such as vegetable or animal oils, fats or waxes, or their components, or mixtures of the same, with oxygen, or gases containing the same, at an elevated temperature at least sufficient to liquefy the aforesaid ingredients in case they should not dissolve in each other and, preferably, in the presence of catalysts as are known to assist the transfer of oxygen. Instead of treating the additions with oxygen, or gases containing the same, conjointly with the initial products prepared from Montan wax, they may be wholly or partially subjected to this treatment beforehand, or be added to the products obtained according to the said applications during the treatment with oxygen, or gases containing the same, or also subsequently to such treatment. The treatment may be carried out, for example, in a vessel which may be provided with filling bodies possessing a large superficial area, such as glass, porcelain or aluminum balls or rings, and by introducing the oxygen or gaseous mixtures containing the same, preferably in a very finely divided state, into the vessel through a suitable inlet at its bottom. The foam leaving the reaction vessel at the top may be introduced again at about the bottom of the vessel.

The products obtained in the manner herein described possess the physical properties of a soft wax of a kind between Japan and carnauba wax, i. e. they are plastic at about 40° centigrade and they are distinguished by

great toughness and ductility when kneaded in contrast to a Montan wax bleached with solutions of oxidizing agents which waxes possess a definite melting point in the neighbourhood of 80° C. below which they are not plastic. The properties of these products can be modified within wide limits by a suitable choice of the working conditions, such as temperature, duration of exposure to the oxygen, or gases containing the same, the nature and amount of the additions and the like. Thus, for example, by raising the temperature and/or duration of working a rather smooth wax can be obtained. Generally, temperatures between 120° and 200° centigrade are employed and preferably those between 140° and 180° centigrade. When working at from 180° to 190° centigrade duration of the treatment is usually from about half an hour to about one hour and a half for the production of products resembling bees wax and from about one to three hours for the production of products of the consistency of Japan wax, depending on the nature of the initial materials when working at 160° to 180° centigrade the time required is about twice to thrice that indicated. Since the acid number of the products is not considerably higher than that of the initial material it can be assumed that no oxidation to carboxylic acids occurs but only a kind of depolymerization and eventual re-condensation.

Moreover, the free carboxyl groups present in the final products so obtained can be wholly or partially neutralized by esterification or by combination with bases or mixtures thereof; or a portion may be esterified, and another portion combined with one or more bases; or the carboxyl groups can be neutralized in other ways, whilst maintaining the CO group, for example with formation of amides, anhydrides and the like in any known and suitable manner, for example in accordance with the aforesaid applications.

A suitable method consists, for example, in subjecting the products to such a treatment that the carboxyl groups of the free fatty acids contained therein chemically combine with other organic acids, in particular other fatty acids or aromatic or hydroaromatic acids, either directly, when one of the components contains free hydroxyl groups, or by a connecting bridge. This may be carried out, for example, by mixing the said materials with oily, fatty, resinous or waxy substances which contain free carboxyl groups and then esterifying the free carboxyl groups present in the acids of the mixture either wholly or partially with polyhydric alcohols or mixtures of the same. The oily, fatty, resinous or waxy substances containing free carboxyl groups may be replaced wholly or partially by aromatic or hydroaromatic acids such as naphthenic acid or salicylic acid and the like or mixtures thereof, and the polyhydric alcohols may be replaced wholly or partially by other hydroxy compounds, for example, hydroxy acids, hydroxy aldehydes, hydroxy ketones, phenols and the like.

The following examples will further illustrate the nature of the said invention which, however, is not limited thereto.

*Example 1*

80 kilograms of a highly bleached product obtained by bleaching Montan wax according to the said application for patent Ser. No. 252,037 are subjected to the action of an air blast in a cylindric vessel which is filled with porcelain rings in such a quantity that the rings protrude above the surface of the liquefied initial materials before the reaction, together with 30 kilograms of paraffin wax and 5 kilograms of castor oil, for 2½ hours at from 160° to 180° centigrade. A product is obtained the physical properties of which resemble bees wax.

*Example 2*

80 kilograms of a Montan wax bleached by means of chromic acid in acetic acid solution are subjected to the action of an air blast, together with 25 kilograms of paraffin wax and 10 kilograms of bleached fatty acids obtained from wool fat, with the addition of 0.1 kilogram of barium cinnamate, for 2 hours at from 160° to 180° centigrade. 100 kilograms of the resulting product are heated with 20 kilograms of polyglycol for 3 hours at from 120° to 130° centigrade and furnish a product which is equal to Japan wax as regards physical properties and, like the latter, can be employed in the production of mixed and saponified creams and the like.

*Example 3*

80 kilograms of a bleached Montan wax are subjected to the action of an air blast together with 30 kilograms of paraffin wax and 5 kilograms of castor oil with the addition of 0.1 kilogram of barium cinnamate, for an hour at 180° centigrade. 100 kilograms of the resulting product are heated with 5 kilograms of the ethylene glycol for from 2 to 3 hours at from 120° to 130° centigrade. 5 kilograms of finely ground barium oxide are then stirred into the melt and heating is continued until the melt has again clarified. The resulting product is as regards its properties something between bees wax and carnauba wax, and can be employed with advantage for tempering the hardness and consistency of boot, or floor polishes and the like.

*Example 4*

80 kilograms of a Montan wax bleached in accordance with the process described in the said application for Patent Ser. No. 254,604, in conjunction with 20 kilograms of paraffin wax, 4 kilograms of wool fat and 1

kilogram of colophony are treated with air for about 2 hours at from 160° to 180° centigrade. The product obtained is a smooth kneadable wax which can be employed in the manufacture of mixed or saponified creams, boot or floor polishes and the like.

*Example 5*

100 parts of a Montan wax highly bleached and then esterified with polyglycol, 20 parts of paraffin wax and, if desired, 5 parts of castor oil are treated at from 160° to 170° centigrade with air for 1½ hours. The product is an almost colorless, soft, wax-like substance which is similar to Japan wax and may be employed for the same purposes as the latter is used.

*Example 6*

70 parts of a Montan wax highly bleached by means of a chromic acid solution, 30 parts of a product obtained by the esterification of the said bleached wax with ethylene glycol; 20 parts of paraffin wax and 5 parts of wool fat are blown with air at 140° centigrade for 1½ hours. The product is an almost colorless, kneadable, flexible wax, which may be used instead of bees wax for many purposes.

*Example 7*

A wax composition is prepared by heating 220 parts of cocoanut fatty acids with 150 parts of ethylene glycol after adding 1 part of 40 per cent sulphuric acid for 1 hour at 120° to 130° centigrade and then adding 1000 parts of a highly bleached Montan wax, 100 parts of stearin and 40 parts of wool grease, whereupon the mass is further heated for about 3 hours to the same temperature. The product obtained is then blown with air for about 30 minutes at from 130° to 140° centigrade. A soft, light-colored wax is obtained which, as regards physical properties, lies between Japan wax and bees wax.

*Example 8*

Montan wax which has been highly bleached with a solution of a quantity of chromic acid which is about 25 per cent higher than is required for simply bleaching the wax, is heated in a cylindric vessel consisting of enamelled metal or of aluminium or of an acid-proof steel to about 160° centigrade and air is introduced through fine nozzles at the bottom of the vessel. After a treatment for one hour the wax which is originally hard, has become kneadable and plastic at about 35° centigrade.

*Example 9*

A Montan wax which has been bleached by means of chromic acid, but not superbleached, is esterified with ethylene glycol and then treated with air in the manner described in the foregoing example whereby a slightly yellow product is obtained, which can be kneaded by the hand and finds useful application in the place of bees wax. By prolonging the treatment for about 1½ hours a product of the plasticity of Japan wax is obtained.

*Example 10*

The free acids contained in a bleached Montan wax are partially esterified with butylene glycol and partially converted into calcium salts in the manner described in the aforesaid application Ser. No. 252,037 and the product obtained is then treated with air as described in Example 8. The physical properties of the final product obtained are between those of bees wax and carnauba wax.

*Example 11*

7 kilograms of fatty acids obtainable from cocoanut oil, 3.5 kilograms of stearin, 5 kilograms of ethylene glycol, 3 kilograms of wool grease, and 90 kilograms of a product obtained by treatment with air at about 160° to 180° centigrade of a mixture of 80 kilograms of a highly bleached Montan wax, 15 kilograms of paraffin wax and 5 kilograms of castor oil, are heated for three hours at from 120° to 130° centigrade. A wax is obtained which is plastic at room temperature.

What we claim is:—

1. The process for the production of products resembling natural waxes which comprises treating a bleached Montan wax in the liquid state for a short time with a gaseous mixture containing oxygen.

2. The process for the production of products resembling natural waxes which comprises treating a liquid mixture of a Montan wax, bleached with a solution of an oxidizing agent, with an organic substance of high molecular weight which has a fluidity not less than that of a plastic for a short time with a gaseous mixture containing oxygen.

3. The process for the production of products resembling natural waxes which comprises treating a Montan wax, bleached with a solution of an oxidizing agent, in the liquid state and in the presence of an oxygen transferring catalyst for a short time with a gaseous mixture containing oxygen.

4. The process for the production of products resembling natural waxes which comprises treating a converted bleached Montan wax in the liquid state for a short time with a gaseous mixture containing oxygen.

5. The process for the production of products resembling natural waxes which comprises treating a liquid mixture of a converted bleached Montan wax with an organic substance of high molecular weight which has a fluidity not less than that of a plastic for a short time with a gaseous mixture containing oxygen.

6. The process for the production of prod-

ucts resembling natural waxes which comprises treating a Montan wax, bleached with a solution of an oxidizing agent and esterified with a polyhydric alcohol, in the liquid state for a short time with a gaseous mixture containing oxygen.

7. The process for the production of products resembling natural waxes which comprises treating bleached Montan wax in the liquid state for a short time with a gaseous mixture containing oxygen, and neutralizing carboxyl groups of the acids present in the product obtained.

8. The process for the production of products resembling natural waxes which comprises treating a Montan wax, bleached with a solution of an oxidizing agent and esterified with a polyhydric alcohol, in the liquid state for a short time with a gaseous mixture containing oxygen, and neutralizing carboxyl groups of the acids present in the product obtained.

9. The process for the production of products resembling natural waxes which comprises treating a liquid mixture of a Montan wax, bleached with a solution of an oxidizing agent and esterified with a polyhydric alcohol, with an organic substance of high molecular weight, which is at least plastic for a short time with a gaseous mixture containing oxygen.

10. The process for the production of products resembling natural waxes which comprises treating a mixture of a Montan wax, bleached with a solution of an oxidizing agent and esterified with a polyhydric alcohol, with a wax at a temperature between 140° and 180° centigrade for a short time with a gaseous mixture containing oxygen.

11. Bleached Montan wax which is plastic at a temperature of about 40° centigrade.

12. Converted bleached Montan wax which is plastic at a temperature of about 40° centigrade.

In testimony whereof we have hereunto set our hands.

WILHELM PUNGS.
KARL BEHRINGER.

# CERTIFICATE OF CORRECTION.

Patent No. 1,834,865. December 1,, 1931.

WILHELM PUNGS ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, line 29, claim 9, strike out the words "is at least" and insert instead has a fluidity not less than that of a; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of October, A. D. 1932.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.