Patented Oct. 7, 1941 2,258,132

UNITED STATES PATENT OFFICE

2,258,132

PERFUME FIXATIVE

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No Drawing. Application May 29, 1940, Serial No. 337,834

2 Claims. (Cl. 167—94)

This invention relates to fixatives in perfume-containing compositions such as toilet and laundry soaps, cosmetics, perfumes and the like. More specifically, this invention relates to hydroxycitronellol and to a process for making it.

It is hardly possible to give an absolutely scientific definition of a fixative, but for practical purposes the following one may be employed. A fixative is a substance which is added to a perfume primarily to decrease the volatility or the rate of evaporation thereof; and if the perfume is a mixture of a number of ingredients having different individual volatilities, the fixative tends to equalize these volatilities so that the odor of the combination does not change materially during the period of evaporation. Obviously, undesirable odor qualities must not be imparted to the perfume by the fixative. It is to be noted also that the foregoing definition includes materials which although technically falling within its scope are nevertheless not satisfactory for the purposes intended.

Fixatives are multitudinous. Satisfactory fixatives are relatively few, however. Bridging the gap between the two requires an unique skill. The element of predictability in perfumery is virtually non-existent. Thus it follows that a skilled perfumer cannot predict whether a given substance will serve as a satisfactory fixative. The fact that the material possesess qualities common to known fixatives, e. g., mild odor or absence of odor, good solubility in perfume ingredients and relatively high boiling point is of little help in ascertaining the suitability of the substance as a fixative. Benzyl benzoate and diethyl phthalate illustrate a case where two compounds having similar physical and chemical properties exhibit different fixative action. The former substance is a satisfactory fixative for most purposes whereas diethyl phthalate is not.

I have made the discovery that hydroxycitronellol prepared by my novel process and whose probable chemical structure is 2,6 dimethyl-octane-diol-2 (or 3), 8 has remarkable fixative properties. It may be incorporated in perfume compositions intended for any purpose, including the perfuming of soaps, cosmetics, industrial products and the so-called handkerchief perfumes. The manner of compounding said perfume compositions and the amounts of hydroxycitronellol to use in a given composition are matters ascertainable by the average skilled perfumer. Naturally, variations in amount of fixative may be made as the nature of the particular problem permits. In general, it has been found that when the weight of hydroxycitronellol corresponds to about 5–20% of the total weight of the compounded perfume oil, as the term is understood in perfumery, satisfactory results are obtained.

My process for making hydroxycitronellol is superior to prior art processes which all have certain material disadvantages. These processes usually employ a metallo-alcoholate such as aluminum ethylate in alcoholic solution as the hydrogenation agent and are conducted by first carefully preparing the hydrogenating agent and then adding the hydroxycitronellal to the alcoholate solution which is contained in a distillation apparatus and maintained at boiling temperatures. It is necessary to regulate the addition of aldehyde very carefully in order to prevent certain undesirable side reactions. Condensation products such as ethers and esters are always formed, thereby reducing the yield of hydroxycitronellol and necessitating steps to saponify or otherwise remove such products. Isolation of the hydroxycitronellol is difficult and involves the solution of the metal present, further heating for 1–2 hours to effect saponification of esters, several washings with hot water to remove the alkali and finally, distillation in vacuo. The best yields obtained are far from theoretical. The processes are time-consuming and admittedly noncommercial, serving only as laboratory methods. The use of costly ingredients such as absolute alcohol also renders such processes undesirable for industrial application.

The process of my invention is a simple and inexpensive one. There are no by-products to remove from the hydroxycitronellol. Consequently, there are no intermediate steps. The yields are substantially theoretical and the method is commercially feasible.

My process is conducted by passing hydrogen gas into a mixture containing hydroxycitronellal and a hydrogenation catalyst such as Raney nickel until absorption of the hydrogen ceases. Other hydrogenation catalysts may be employed instead of Raney nickel. An organic liquid which is a solvent for hydroxycitronellol and hydroxycitronellal may be used to dilute the reaction mixture sufficiently to facilitate operations by reducing the viscosity of the mixture. Lower aliphatic alcohols, ethyl acetate, dibutyl ether and dioxane are some examples of such liquids which are also required to be inert under the reaction conditions. Atmospheric or elevated pressures may be employed. Temperatures between room temperature and the boiling point of the

reaction mixture can be used. However, 20°–100° C. is the preferred range. Hydroxycitronellal is quite viscous below 20° C., a condition not conducive to satisfactory gas absorption or reaction operations. Above 100° C. the stability of hydroxycitronellal is the limiting factor. Suitable bubbling means are provided when possible to indicate whether hydrogen is being absorbed in the reaction mixture.

After absorption of hydrogen has ceased the flow of hydrogen is stopped, the catalyst is allowed to settle, the supernatant liquid is withdrawn and the solvent, if any, is removed. The hydroxycitronellol is distilled, preferably under reduced pressure. After a small forerun, a colorless and somewhat viscous oil having a mild, pleasant odor and characterized by the following physical constants is obtained.

Boiling point	140° C./4 mm. mercury pressure
Specific gravity at 25° C./25° C.	0.930
Refractive index n_D^{20}	1.460

Upon acetylation, the oil yields a diacetate which is a colorless, nearly odorless oil, which is not as viscous as the diol and which has the following constants:

Boiling point	132° C./3 mm. mercury pressure
Specific gravity at 25° C./25° C.	0.9618
Refractive index n_D^{20}	1.329

An alternative method may be employed, when desired, in the preparation of mixtures of hydroxycitronellal and hydroxycitronellol. In this method, all of the steps are the same as before but the hydrogen is stopped when a predetermined amount of the gas, less than that required for reduction of all of the hydroxycitronellal to hydroxycitronellol, has been absorbed. The amount of hydrogen used depends on the ratio of aldehyde to alcohol desired in the mixture. For example, if an equimolecular mixture of hydroxycitronellal and hydroxycitronellol is desired then 1 mol of hydrogen is used for every 2 mols of aldehyde originally present.

Example #1

In an experiment, 20 parts of Raney nickel catalyst were added to 480 parts of 2,6 dimethyl-octane-ol 2 (or 3)-al-8 and 960 parts of alcohol; hydrogen gas was then passed into the mixture while agitating the suspension vigorously. Atmospheric pressure and a temperature of about 60° C. were employed. Hydrogen addition was continued for 6 hours until absorption thereof practically ceased. After the catalyst and alcohol had been removed, 455 grams of hydroxycitronellol having the properties before noted were obtained. The yield corresponds to 94.3% of the theoretical, based upon the weight of hydroxycitronellal employed.

Example #2

900 pounds hydroxycitronellal and 10 pounds Raney nickel catalyst are charged into a suitable pressure reaction vessel. Hydrogen gas is introduced while maintaining the temperature of the reaction mixture at 55–60° C. The initial hydrogen pressure of 50 pounds is gradually increased as the reaction progresses until a final pressure of 150 pounds is reached, in order to affect a reasonable speed of operation. When approximately 1,800–1,900 cubic feet of hydrogen have been introduced, the absorption rate becomes negligible and the reaction is considered finished. This usually requires from 48 to 72 hours. Excess hydrogen pressure is released and the catalyst removed by filtration to yield 910 to 920 pounds crude hydroxycitronellol. This is subsequently refined by distillation, preferably in vacuo, to give 855 pounds of hydroxycitronellol, or a yield of 95% on hydroxycitronellal.

Hydroxycitronellol is soluble in the alcohols, esters, ethers, ketones, phenols, lactones, etc. which are commonly used in perfumery. It is also soluble in practically all essential oils except those which are predominantly terpenic. It is not appreciably soluble in hydrocarbons such as benzene, naphtha, etc.

It should be noted in the above formulation that the alternative position 2 or 3 is given for one of the hydroxyl groups. This is done because it is not known whether dimethyl octane-ol-al which is used as the starting material in my process has the hydroxyl group in the 2 or 3 position or whether it is a mixture of the two products. The same uncertainty exists in the dimethyl octane diol. Hydroxycitronellol when used herein means the substance having the beforementioned physical and chemical properties and whose probable chemical formula is 2,6 dimethyl-octane-diol-2 (or 3), 8.

The foregoing illustrates the practice of my invention which, however, is not to be limited thereby but is to be construed as broadly as permissible in view of the prior art and limited solely by the appended claims:

I claim as my invention:

1. Perfume-containing compositions having hydroxycitronellol as a fixative ingredient.

2. Perfume-containing compositions having 5–20% by weight of hydroxycitronellol as a fixative ingredient, said weight being based on the total amount of compounded perfume oil in said compositions.

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