

UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING VANILLIN.

SPECIFICATION forming part of Letters Patent No. 754,164, dated March 8, 1904.

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To all whom it may concern:

Be it known that I, ROBERT N. RIDDLE, a citizen of the United States, residing at Uwchland, Chester county, State of Pennsylvania, have invented certain new and useful Improvements in Processes of Producing Vanillin from Acet-Iso-Eugenol, of which the following is a full, clear, and exact description.

My invention relates generally to the production of vanillin, and particularly to the method of producing the acet-vanillin by the oxidation of the acetyl compound of iso-eugenol.

The object of the invention is to improve the method or process of producing vanillin, wherein the employment of the dangerous solvents heretofore employed for dissolving the acet-iso-eugenol shall be dispensed with and their place supplied by a new solvent the employment of which not only eliminates the element of danger, but has the positive function and effect of producing a better or rather purer quality of vanillin and a greater yield from a given quantity of iso-eugenol acted on, and consequently at less cost of production. My invention does not comprise any change in the oxidizing step, which remains the same as heretofore practiced.

Heretofore vanillin has been made by dissolving the acetyl compound of iso-eugenol by the employment of ethyl ether or benzene as the solvent, then oxidizing the same by means of a chromic-acid solution, and finally removing the acetyl group by means of an alkali. One objection to the use in the first step of such solvents as those named above is because of their volatile and highly-inflammable nature, creating liability to dangerous explosion and fire because of their low boiling-point and the necessity for constantly agitating them mechanically-inflammable vapors are given off in great abundance, the mechanical agitation being essential because of their immiscibility with the aqueous layer in the subsequent oxidizing step in the bichromate solution. Another objection to their use as such solvent affecting the end product is that their volatility makes it well-nigh im-

possible to reach the temperature which is necessary for the full oxidation of the acet-iso-eugenol in order to get the best and purest yield of acet-vanillin. Still another objection to such solvents, (which, however, applies only to benzol,) namely, the insolubility of the chromic acid therein, is a great disadvantage, because it makes indispensable a thorough and constant mechanical agitation in order to obtain any satisfactory action of the oxidizing agent on the acet-iso-eugenol. Aside from these objections stated to the use of such solvents the yield of acet-vanillin when they are employed is only moderate. They are comparatively expensive for the reason stated, highly dangerous to use in this process, wasteful of the compound acted on by reason of incomplete oxidation of the mass, and the ultimate result is a less desirable end product.

My invention consists of a modification of this process whereby all these difficulties and objections are overcome; and it consists of changes in the first step—namely, the employment as a solvent of the starting material (the acet-iso-eugenol) of the ester of a fatty acid—for example, amyl acetate—in lieu of the volatile solvents heretofore employed. In addition to its not being open to the objections named the ester of a fatty acid used as a solvent has decided advantages. Among others, it dissolves the acetyl compound completely, which is a valuable quality, as the starting material to be dissolved is a comparatively valuable raw material, while an equally advantageous feature is that the chromic acid present in the oxidizing solution is soluble in it, and so is brought into more intimate contact with the dissolved acet-iso-eugenol, while the chromium salt formed as the result of the oxidation reaction is nearly insoluble in the amyl acetate and passes into the aqueous layer, in which it is perfectly soluble. Thus the oxidation proceeds more easily, is more complete, and the yield of acet-vanillin is much larger, very often amounting to as much as and occasionally exceeding seventy-five per cent. of the acet-iso-eugenol employed. Another advantage results from the higher boil-

ing-point of most of these esters of fatty acids. Thus amyl acetate boils at 148° centigrade, (298.4° Fahrenheit,) and ethyl butyrate, another of the class, boils at 120° centigrade, 5 (249.6° Fahrenheit,) and, as is obvious to a chemist, these higher boiling-points make it possible to carry on the oxidation of acet-iso-eugenol at a much higher temperature than would be possible with highly volatile and inflammable solvents, such as ethyl ether and benzene, and in consequence the yield of acet-vanillin is increased and improved. 10

In carrying out my improved process practically I have found that twenty-five pounds 15 of acet-iso-eugenol will be satisfactorily dissolved in two hundred and fifty pounds of amyl acetate; but I wish it to be understood that other fatty-acid esters, such as ethyl acetate and amyl butyrate, may be substituted 20 for amyl acetate. For the oxidation of such a dissolved quantity, free chromic acid in solution or its equivalent, found in fifty-five pounds of sodium or potassium bichromate dissolved in one hundred and twenty-five 25 pounds of sulfuric acid, to which in making up the bath three hundred pounds of water is added. The dissolved acetyl compound should be agitated in this oxidizing solution. It must also be understood that variations within 30 reasonable limits may be made in the proportions stated in the example given without substantially departing from and without loss of the recited advantages to be derived therefrom in the production of acet-vanillin from

acet-iso-eugenol. The acetyl-vanillin compound is then to be decomposed by withdrawing the acetyl group and the residual vanillin purified in the customary manner, as before stated. 35

Having thus described my invention, what I claim as new, and desire to secure by Letters Patent, is— 40

1. The process of producing acet-vanillin from acet-iso-eugenol, which consists in submitting to the action of suitable oxidizing 45 agents a solution of acet-iso-eugenol which has been dissolved in the ester of a fatty acid.

2. The process of producing acet-vanillin which consists in preliminarily preparing a saturated solution of acet-iso-eugenol by 50 means of the ester of a fatty acid as a solvent, then oxidizing the same by a chromic-acid solution.

3. The process of producing vanillin which consists in dissolving acet-iso-eugenol in the 55 ester of a fatty acid, then oxidizing the same by means of a chromic-acid solution, then purifying the resultant acet-vanillin by isolating the acetyl compound, and freeing the vanillin therefrom. 60

In testimony whereof I have hereunto affixed my signature this 9th day of June, A. D. 1903.

ROBERT N. RIDDLE.

Witnesses:

A. FLORENCE YERGER,
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