

UNITED STATES PATENT OFFICE

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CARBONYL COMPOUND AND PROCESS OF PREPARING THE SAME

No Drawing.

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This invention relates to improvements in the manufacture of oxygen-containing organic compounds from hydrocarbons of the type of petroleum. The invention will be fully understood from the following description, in which particular reference is made by way of illustration to the treatment of petroleum oil for the production of the higher aldehydes.

I have found that aldehydes may be economically prepared from petroleum hydrocarbons, for example straight-run or cracked gasoline, by a series of reactions including the production of olefins, the conversion of the olefins into chlorhydrins, and the transformation of the chlorhydrins into aldehydes.

The olefins may be produced by passing the hydrocarbon stock in vapor form through a heated zone, together with a regulated amount of air or oxygen. The stock is preferably gasoline, but may be any petroleum hydrocarbon mixture containing no substantial amount of components heavier than those normally occurring in kerosene. When air is used it should ordinarily be injected at a rate of about 5 to 20 cubic feet per pound of hydrocarbon. The temperature is kept below the usual cracking range of about 725° to 875° F. Temperatures between 300° and 650° F. are generally suitable for my purpose.

Steam may be introduced as a temperature modifier, or for other purposes, if desired. Steam injection is particularly useful if undiluted oxygen instead of air is employed. Atmospheric pressure is recommended, except for stocks of high vaporizing temperature. With such stocks it is often desirable to reduce the pressure to an amount sufficient to ensure vaporization without cracking.

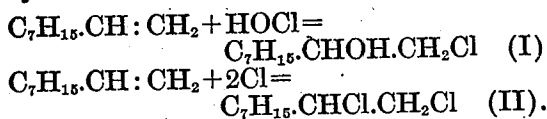
From the heated zone the vapors pass to a condenser system. When desired, the products may be treated to remove any gum-

forming constituents that may be present. Washing with water, or with an acid or alkali solution, or steaming, are suitable in this connection.

The method of preparing olefins does not form an essential part of the present invention, and any other suitable method may be substituted for that given above. The product prepared as described, or in a similar manner, will contain substantial quantities of the normal hydrocarbons of the olefin series, especially pentylene and the members of the olefin series up to and including decylene. Unsaturated compounds of greater complexity may also be formed in small amount. These are not detrimental for most purposes, but the simpler olefins are of chief importance for my purpose.

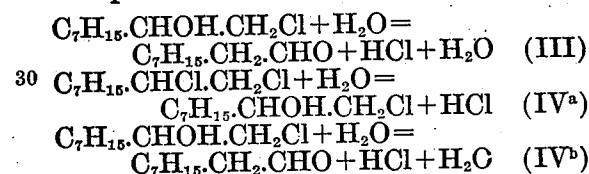
In some cases gasoline prepared by cracking methods contains a sufficient amount of olefin material to make it directly suitable for treatment by my process. In accordance with the present invention, the olefins are first converted into chlorhydrins. The method consists in stirring the olefins at low temperature, say about 0° C., with a dilute solution of hypochlorous acid. As a rule, the hypochlorous acid solution should not be stronger than 1%, if formation of dichlorids is to be avoided. However, in my process the chlorhydrins form only an intermediate product and are later transformed into aldehydes by heating with water. Dichlorids are therefore not objectionable, since they react similarly to the chlorhydrins when so treated. This is an advantageous feature of the process, since no precaution need be taken to avoid the formation of dichlorids. Higher and more reactive concentrations of hypochlorous acid may accordingly be used. While the chlorinating method described is preferred, any method which furnishes chlorhydrins, or mixtures of chlorhydrins and dichlorids, will serve. I use the term "chlorhydrin" as meaning a glycol ester of

hydrochloric acid. Selecting nonylene as illustrative of the olefins being treated, the reactions for the formation of chlorhydrin and dichlorid may take place as represented by the following equations:



10 Pentylene and in general all the olefins formed as described and of greater molecular weight than pentylene appear to react in the same manner. It is to olefins of greater molecular weight than butylene, not to those which are gaseous or vaporous at room temperature, that my invention relates.

15 The chlorhydrin or mixture of chlorhydrins, or mixture of chlorhydrins and dichlorids, is converted into aldehydes by heating with water. The olefin material and water should be brought into intimate contact and heated to about 110° to 200° C. for a period of about one to three hours in a closed vessel. The following equations are illustrative of the type of reaction that may take place:



35 The higher aldehydes have heretofore been made only by laborious and costly methods. They may be prepared economically and in a state of substantial purity by the process disclosed herein. Fractionation under vacuum suffices to separate the aldehydes from unchanged chlorhydrins, dichlorids, and other compounds that may be present. The aldehydes are useful as starting materials for the preparation of a wide variety of compounds and are valuable in themselves as fixatives in the perfume industry and for other purposes.

40 If the double bond of the olefin is not at the end of the hydrocarbon chain, then a ketone is obtained by heating the corresponding chlorhydrin derivative with water. However, my experiments show that the olefins obtained by the above described oxidation process, or in cracking, contain the double bond mostly at the end of the hydrocarbon chain. Therefore, only an inconsiderable amount of ketones is formed.

45 An important feature of my invention is the improvement of motor fuel by addition of aldehyde material. For this purpose the aldehydes may be prepared separately and blended with the fuel, or they may be prepared directly in the fuel. For example, when a cracked gasoline containing a relatively high percentage of olefin material is

70 treated with hypochlorous acid or other suitable chlorinating agent for the production of chlorhydrins, and with water for the production of aldehydes, as described above, a gasoline of much improved character is obtained. It has a pleasant odor and a substantially less tendency to produce knocking or detonation than the untreated gasoline.

75 The aldehydes have, as a rule, a higher boiling point than the hydrocarbons from which they are formed. There is accordingly some elevation of the boiling point range of the fuel, but this is not an important objection, since the increase of boiling point range may be compensated for by the addition of lighter gasoline, which will be retained on account of the high fixative power of the aldehydes. Ordinarily, carbonyl compounds, whether aldehydes or ketones, are suitable as an anti-knock agent in motor fuel.

80 It will be understood that my invention is not restricted by any theoretical considerations in the foregoing description and that various changes and alternative procedures may be adopted within the scope of the appended claims, in which it is my intention to claim all novelty inherent in the invention as broadly as the prior art permits.

I claim:

95 1. Process of preparing carbonyl compounds of hydrocarbons, comprising treating olefins of greater molecular weight than butylene with hypochlorous acid, whereby chlorin-containing compounds are formed, and transforming the chlorin-containing compounds into carbonyl compounds by heating with water.

100 2. Process of preparing aldehydes from hydrocarbons liquid at room temperature and having a molecular weight not greater than that of hydrocarbons normally present in gasoline and kerosene, comprising converting at least a portion of said hydrocarbons into olefins, treating the olefins with hypochlorous acid, whereby chlorhydrins are formed, and converting the chlorhydrins into aldehydes by heating with water.

105 3. Process of forming carbonyl derivatives of hydrocarbon compounds in a mixture of olefin and non-olefin hydrocarbons liquid at room temperature and having a molecular weight not greater than that of hydrocarbons normally present in kerosene, comprising treating the mixture with a chlorinating agent to convert the olefins into chlorin-containing compounds, and converting the chlorin-containing compounds into carbonyl compounds by heating with water.

110 4. Process of forming aldehydes in a gasoline containing olefins, comprising treating the gasoline with hypochlorous acid, and converting the resulting chlorinated substances into aldehydes by heating with water.

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