This invention relates to processes of preparing higher fatty aldehydes and it comprises processes wherein a metal soap or salt, such as alkali metal salts, alkaline earth metal salts, zinc salts, copper salts, and the like, of higher fatty acids, are reacted with formaldehyde; it further comprises processes wherein such soaps or salts are reacted with formaldehyde in the presence of steam, and, if desired, in the presence of catalysts of an oxidizing nature such as metal oxides of the fifth and sixth groups of the periodic system.

In the United States patent Number 2,033,539, in the names of Ralston and Jackson, there are described processes of preparing higher fatty aldehydes from higher fatty acids by reacting such fatty acids, while in vapor phase, with formaldehyde in the presence of oxidizing catalysts. That process is a marked step forward in the art since by it fatty acids or esters thereof can be directly converted to their corresponding aldehydes. Before the discovery of this method there was no process available which could be used commercially for the conversion of the higher fatty acids to aldehydes. The classical reaction between a calcium soap and calcium formate is of no commercial significance when dealing with higher fatty acids. These fatty acids are all phatic carboxylic acids having at least six carbon atoms and are acids commonly found in fats and fatty oils. Although the calcium formate reaction will work fairly well with low molecular weight fatty acids, for example butyric or propionic, it is useless when dealing with the higher fatty acids which react sluggishly and yield various by-products and decomposition products as the result of side reactions.

The patented process referred to above overcomes many of the disadvantages observed in the calcium formate method and permits higher fatty aldehydes to be prepared at low cost and in high yields. As a result, these aldehydes have become available commercially and from them many valuable organic materials can be prepared. For example, the aldehydes can be reduced to alcohols and the alcohols then sulfonated to form valuable wetting-out agents. The aldehyde group is extremely reactive. Since it is, in the higher fatty aldehydes, attached to relatively heavy alkyl radicals, these aldehydes offer ways of introducing such alkyl radicals into chemical compounds. Hitherto ways of alkylating so that the introduced alkyl group was of relatively high molecular weight have been limited to a very few methods of doubtful value commercially.

The said patented process requires that the higher fatty acid (or its ester) be vaporized and contacted with formaldehyde at a rather high reaction temperature, generally about 400° C., and at least above the boiling point of the fatty materials under the prevailing pressure conditions. The patented process also requires the presence of oxidizing catalysts. Under these conditions there is, of course, some tendency for the fatty acid to decompose to give tars, lower aldehydes, and other by-products generally of no use. When carefully controlled the process works very well, but, being vapor phase throughout, that is to say, all reactants (other than catalyst) are in the vapor condition, there are technical difficulties which are not associated with liquid or solid phase reactions.

Consequently we have set ourselves to the problem of developing a way of converting higher fatty acids to their corresponding aldehydes which avoids a vapor phase reaction. We have discovered that fatty acid soaps derived from the higher fatty acids can be made to react with formaldehyde vapor. This means that we can react the solid soaps with vaporous formaldehyde at a moderately elevated temperature and condense a liquid consisting largely of an aldehyde corresponding to the fatty acid of the soap treated. In the process of the present invention the reaction temperature can be much below the boiling point of the fatty acid from which the metal soap is made. Consequently the present process avoids any thermal conditions which might lead to "cracking" the fatty acid with the resultant formation of tars and other undesirable by-products. Moreover no catalyst is necessary, although we do not wish to exclude a catalyst. Under some conditions, as when dealing with fatty acid soaps which seem to resist conversion to aldehydes at reasonably low temperatures (generally 200° to 300° C.) a small amount of an oxidation metal oxide catalyst can be admixed with the soap before treating with formaldehyde. Suitable catalysts are those described in the aforementioned Ralston and Jackson patent. These are metal oxides of the fifth and sixth groups, such as manganese oxide, vanadium oxide, chromium oxide, molybdenum oxide etc. Manganese oxide, however, is an oxide of a metal in the seventh group and forms an exception to the rule that those oxides of metals in the fifth and sixth group are best. Various mixtures of oxides can be used and generally the amount admixed with the soap is very small; one percent is usually sufficient.
In the present process we find it advantageous to have steam present along with the formaldehyde vapor. This helps to steam-distill the aldehydes formed by reaction between the metal soap and the formaldehyde. Consequently any tendency for the higher fatty aldehydes to decompose is avoided by this expedient. Steam can be omitted if desired, but little or no extra expense is involved in including it. Perhaps the cheapest source of formaldehyde is the ordinary aqueous solution thereof available commercially. Hence, when we boil this solution to liberate formaldehyde, we form quantities of water vapor at the same time and the mixture of water vapor and formaldehyde is advantageously led directly into contact with the soap.

All of the soaps which we treat with formaldehyde are, of course, normally solid. Hence they can be supported in layers in a reaction vessel and formaldehyde vapor passed through the layers. Or a tower can be loosely filled with the soap admixed with an inert porous material like coke to expose large surface areas to contact with the formaldehyde. Some of the soaps, such as the alkaline metal soaps may tend to liquify during the reaction, especially if much water be present. This is not to be regarded as a disadvantage since the formaldehyde will react readily with the liquid soap. Likewise the soap of many fatty acids, such as oleic, are liquids at moderately elevated temperatures, and in this case, our process can be considered a mixed liquid and vapor phase reaction. But only the formaldehyde (and steam when present) is a vaporous reactant.

In substance then, our invention comprises processes of reacting soaps with formaldehyde. The reaction can be written schematically as follows, assuming that a calcium soap is used:

$$\text{RCOO}_2\text{Ca} + \text{HCHO} \rightarrow 2\text{RCCHO} + \text{CaCO}_3$$

Obviously the reaction is probably much more complex than the simple statement given above. But the reaction expresses the beginning and end products. Any steam present during the reaction appears to have no effect other than aiding in the vaporization and distillation of the aldehydes. When alkaline metal soaps are used the reaction can be written as follows:

$$2\text{NaCOO}_2 + \text{HCHO} \rightarrow 2\text{RCCHO} + \text{Na}_2\text{CO}_3$$

Advantageously an excess of formaldehyde over that required by theory is used.

Before describing our invention with reference to the treatment of specific soaps we shall indicate its breadth. Our process is applicable to the conversion of all soaps derived from higher fatty acids. By higher fatty acids we mean those fatty acids having at least six carbon atoms. Among them are caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric, carbamino, cerotic, melissic, oleic, linoleic and linolenic. Soaps made from crude lard fatty acids are especially advantageous since the fatty acid source is abundant and cheap. Likewise the metal of the soap can be any metal. All of the soaps of alkaline-forming metals are operative. These comprise soaps of sodium, potassium, calcium and barium as typical examples of the alkaline-forming metal soaps. Soaps of zinc, copper and iron are operative and we have no reason for believing that there are any soaps which are impervious in our process. Of the many soaps available the cheapest are those derived from calcium since the fatty acids can be readily converted to calcium soaps by treatment with lime. Consequently we find it more advantageous to use calcium soaps and we shall describe our invention with specific reference to the treatment of these soaps.

It would serve no useful purpose for us to describe specifically the conversion of all of the many metal soaps of higher fatty acids to their corresponding aldehydes. Consequently we shall limit our description to the conversion of laurate to lauraldehyde. The procedure is precisely the same when treating stearates, palmitates, myristates and other salts of higher fatty acids.

For example, we charge a suitable reaction vessel with 100 parts by weight of calcium laurate and heat the contents to a temperature of 200° to 300° C. Generally about 275° C. will be found about the best. Then we vaporize 3000 parts by weight of a commercial formalin solution consisting of 40 percent formaldehyde and 60 percent water and pass these vapors into the reaction vessel.

Vapors leaving the reaction vessel are condensed. The condensate consists of an aqueous layer composed of unreacted formalin and an oily layer composed of lauraldehyde and any products of side reactions. This oily layer amounts to 40 parts by weight. Advantageously we wash it with water, dissolve it in ether or other solvent which is immiscible with water, extract the solution with dilute caustic soda solution to remove any traces of acidic materials, remove the solvent, and fractionate the remaining oily layer. Most of the product is lauraldehyde but it contains small quantities of methyl laurate and laurone, a ketone.

Under similar conditions of temperature and quantities, sodium laurate gives substantial yields of lauraldehyde, barium stearate gives substantial yields of stearaldehyde and calcium palmitate yields palmaldehyde. As the molecular weight of the fatty acid constituent of the soap decreases a moderate increase in side reactions is noted but this can be corrected by operating at somewhat lower temperatures, about 200° to 225° C. In any event it is advantageous to keep the reaction temperature as low as possible and consistent with reasonably rapid reaction velocity.

Instead of using formalin solution we can, of course, use gaseous formaldehyde or formaldehyde-yielding materials such as metal para-formaldehyde but in most cases we prefer to use commercial formalin since it is cheap and its water content, which vaporizes along with the formaldehyde, prevents the decomposition of the higher fatty aldehydes and aids in the rapid removal of them from the reaction zone.

In the appended claims we use the language “soap of a fatty acid having at least six carbon atoms” to denote the many soaps which we have described. Likewise the term “formaldehyde” embraces formaldehyde present during the reaction regardless of its original source, be it formalin, or meta or para formaldehyde, or other substances yielding formaldehyde at the reaction temperature.

Having thus described our invention what we claim is:

1. The process of preparing aldehydes which comprises passing gaseous formaldehyde into contact with a body of a soap of a fatty acid having at least six carbon atoms, the soap being maintained at a moderately elevated temperature
sufficiently high to induce reaction between the formaldehyde and the soap.

2. The process of preparing aldehydes which comprises passing gaseous formaldehyde and water vapor into contact with a body of a soap of a fatty acid having at least six carbon atoms, the soap being maintained at a moderately elevated temperature sufficiently high to induce reaction between the formaldehyde and the soap.

3. The process of preparing aldehydes which comprises passing gaseous formaldehyde free of oxidizing gases into contact with a body of a soap of a fatty acid having at least six carbon atoms admixed with an oxidation catalyst, the soap being maintained at a moderately elevated temperature sufficiently high to induce reaction between the formaldehyde and the soap, and oxidizing conditions being absent.

4. The process as in claim 1 wherein the soap is an alkali-forming metal soap.

5. The process as in claim 2 wherein the soap is an alkali-forming metal soap.

6. The process as in claim 3 wherein the soap is an alkali-forming metal soap.

7. The process as in claim 1 wherein the soap is a calcium soap.

8. The process as in claim 2 wherein the soap is a calcium soap.

9. The process as in claim 3 wherein the soap is a calcium soap.

10. The process of preparing lauraldehyde which comprises passing gaseous formaldehyde into contact with a body of calcium laurate maintained at a moderately elevated temperature to induce reaction between formaldehyde and the calcium laurate.

11. The process of preparing aldehydes which comprises passing gaseous formaldehyde into contact with a body of an alkali-forming metal soap of a fatty acid having at least six carbon atoms, the soap being maintained at a temperature of about 200° C. to about 300° C.

12. The process of preparing aldehydes which comprises passing gaseous formaldehyde and water vapor into contact with a body of an alkali-forming metal soap of a fatty acid having at least six carbon atoms, the soap being maintained at a temperature of about 200° C. to about 300° C.

13. The process of preparing aldehydes which comprises passing gaseous formaldehyde free of oxidizing gases and water vapor into contact with a body of an alkali-forming metal soap admixed with an oxidation catalyst, the soap being maintained at a temperature of about 200° C. to about 300° C., and oxidizing conditions being absent.

ANDERSON W. RALSTON.
ROBERT J. VANDER WAL.