

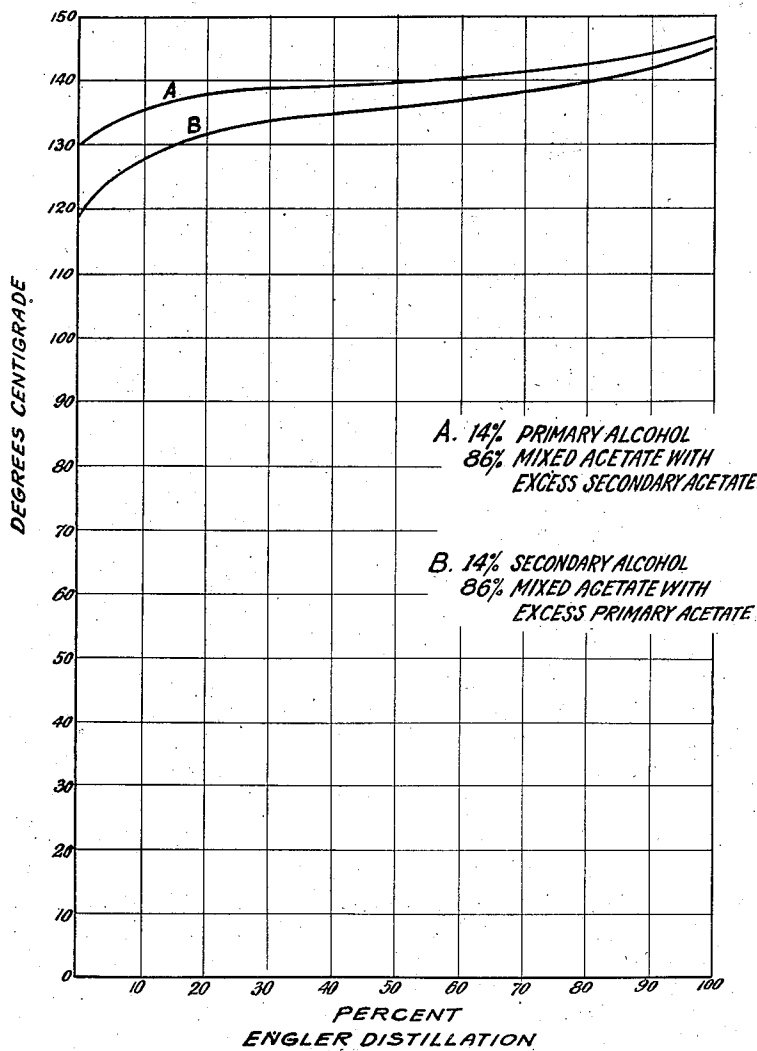
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ESTERIFICATION

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UNITED STATES PATENT OFFICE

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ESTERIFICATION

Application filed February 4, 1927. Serial No. 165,878.

My invention relates to esterification of alcohols and particularly to the production of mixtures containing esters of alcohols and alcohols and having a desired boiling range.

5 A special application of my invention resides in the production from mixtures of alcohols, of a mixture of esters and alcohols that has a higher boiling range than a similar mixture produced by the ordinary processes of esterification, a special feature of my invention being the production of a mixture of alcohols and esters that is substantially free of the lower boiling alcohols contained in the original mixture esterified. A very important commercial aspect of my invention is that it is possible to produce thereby mixtures of esters and alcohols in commercially desired proportions and in which the alcohol fraction of the mixtures consists mainly of the higher boiling alcohols of the alcohol mixture from which the final mixture is produced.

My invention relates to the esterification of mixtures of alcohols composed of various constituents. The mixture of alcohols esterified in accordance with my invention may be a mixture of several primary alcohols of different boiling points and containing different numbers of carbon atoms, or a mixture of several secondary alcohols of different boiling points and having the same number of carbon atoms, or a mixture of primary and secondary alcohols having the same number of carbon atoms, or a mixture of primary alcohols respectively having the same number of carbon atoms, or practically any mixture of alcohols. Special mixtures of alcohols, the esterification of which falls within my invention, are various mixtures of primary and secondary amyl alcohols primary and secondary butyl alcohols, and primary and secondary hexyl alcohols, such mixtures including the mixtures of alcohols obtained by the hydrolysis of corresponding chlorine substitution products. Other mixtures of alcohols from which commercially important mixtures of esters and alcohols may be produced may be made up to suit requirements, a special example being a mixture of ethyl and butyl alcohols.

I have found that the separation of alcohols of different boiling points may be carried out by rectification in the presence of their esters in spite of formation of constant boiling mixtures comprising alcohols and esters. And, I have found that this property of alcohols may be advantageously utilized in the preparation of ester-alcohol mixtures of desired composition and of commercial superiority.

In accordance with my invention a mixture of alcohols is esterified which contain the alcohols that are desired in the final mixture and also the alcohols from which the esters desired in the final mixture are produced. If the esterification of a mixture of alcohols is carried as far as possible in a single operation the products thereof will include esters and a residue of the lower boiling alcohols, causing the products of esterification to have high vapor pressure and a relatively low boiling range and a relatively large spread between initial and final boiling points. However, commercial requirements are such that it is desirable to have the alcohol fraction of the ester-alcohol mixture consist as far as possible of higher boiling alcohols and desirable that the mixture shall have a relatively high boiling range and low vapor pressure and a relatively small spread between the initial and final boiling points. As a specific example, it is pointed out that if an ester-alcohol mixture consisting of about 14% amyl alcohol and the balance of amyl esters, a proportion well suited to commercial requirements, is produced in one esterifying step from a suitable mixture of amyl alcohols, the alcohol fraction of the mixture will consist mainly of the lowest boiling alcohols present in the original mixture, whereas the ester-alcohol mixture is much more suitable to commercial requirements if the alcohol fraction thereof consists mainly of higher boiling alcohols of the original amyl alcohol mixture.

An important feature of my invention is the production of ester-alcohol mixtures in which the alcohol fraction consists of higher boiling alcohol present in the original alcohol mixture. In accordance with my inven-

tion, after a suitable mixture of alcohols is made, the alcohol mixture is esterified to a degree less than that desired in the finished product, e. g., to a point at which the alcohol fraction constitutes about 30% of the mixture in a case where the alcohol fraction of the final mixture is to be about 14% thereof. The next step in the practice of my invention consists of removing from the products of the esterifying step, by rectification, lower boiling alcohols. Inasmuch as the alcohols form constant boiling mixtures with their esters, some of the lower boiling esters pass off with the lower boiling alcohols. The residue will consist of esters in the desired proportion with an alcohol fraction composed chiefly, if not entirely, of higher boiling alcohols.

A further feature of my invention consists in mixing the fraction separated by rectification, with an additional quantity of the alcohol mixture and then repeating the esterifying and rectifying step of my process, and if desired, continuing the process consisting in mixing the separated fraction of each rectifying operation with additional fresh alcohol mixture and then esterifying and rectifying. In the practice of my invention the residues of successive rectifying operations may be brought together or kept separate and those residues may be purified by distillation to eliminate undesirable color and any decomposition products formed. In the practice of my invention the residue of the first rectification is such that the ratio of lower boiling alcohol to higher boiling alcohol is less than it is in the original alcohol mixture and the ratio of higher boiling esters to lower boiling esters is greater than the ratio of higher boiling alcohol to lower boiling alcohol in the original alcohol mixture; and separated fractions of all rectification steps are such that the ratio of lower boiling alcohols to higher boiling alcohol is greater than it is in the original alcohol mixture and the ratio of higher boiling esters to lower boiling esters is much less than the ratio of higher boiling alcohol to lower boiling alcohol in the original alcohol mixture.

As the fractions separated by rectification are successively mixed with fresh alcohol mixture in preparation for the succeeding esterifying step, the operation reaches an equilibrium, and because of the return of the head products of rectification to successive esterification steps the residues of the successive rectifications, after the first, are such that the ratio of higher boiling esters therein to lower boiling esters therein is less than the ratio of higher boiling alcohols to lower boiling alcohol in the original alcohol mixture. This condition occurs because the higher boiling alcohol of the original alcohol mixture is so largely used up in forming the alcohol fraction of the ester alcohol mixtures.

Ester-alcohol mixtures produced in accordance with my invention, in comparison with similar mixtures produced by esterification in a single step, have the same ester content but have a lower vapor pressure and are substantially free of lower boiling alcohols. This is shown by a numerical example: beginning with the mixture containing 70% of primary amyl alcohol and 30% of secondary amyl alcohol and producing a final product having 86% of amyl acetates, acetylation in a single step produces a final product containing an alcohol fraction of which 70% is primary alcohol and an acetate fraction of which 70% is primary amyl acetate, whereas production of a final product containing 86% of amyl acetate in accordance with my invention from the same original mixture gives a product in which the alcohol fraction is substantially 100% primary alcohol and the acetate fraction consists of 64% primary acetate. Any undesirable effect resulting from reduction of the primary acetate percentage from 70 to 64 is very much more than compensated for by the substantial elimination of secondary amyl alcohol from the alcohol fraction. In commercial acetylation the prime object is to obtain as high a conversion as possible of the acetic acid employed. By seeking only partial acetylation this object is attained because of the unusually large excess of alcohol, whereas in seeking a maximum degree of esterification the alcohol excess is reduced or the acetic acid may even be present in excess. Excess alcohol is easily recovered but when the excess is reduced the rate of reaction is low and when acetic acid is in excess its recovery is difficult. In general, in the production, in accordance with this invention, of a mixture of alcohols and esters, in which the esters constitute a desired proportion of the mixture, a mixture of alcohols having respectively different boiling points is subjected to esterification, and there is thereby produced a mixture of alcohols and esters in which the proportion of esters is not as high as the proportion of esters desired in the final product. Then, by rectification, lower boiling alcohols are removed, and that operation incidentally carries away from the residue some of the lower boiling esters, but the rectification is continued until the proportion of esters in the residue has been increased, by removal of alcohols, to the proportion desired in the final product. The proportion of esters desired in the final product will ordinarily be determined by the requirements of the trade in which the ester-alcohol mixture is employed. For example, in the lacquer trade an ester-alcohol mixture comprising 85 per cent. of esters has been employed, and there is some demand for an alcohol-ester mixture comprising 90 per cent. of esters when butyl esters and alcohols make up the mixture.

When the ester-alcohol mixture is made up of amyl alcohols and esters, a mixture comprising 88 per cent. of esters is a mixture of high quality. In producing such a mixture, the esterification will be continued until the esters constitute substantially less than 88 per cent. of the mixture, and then by rectification lower boiling alcohols and some lower boiling esters are removed, with a consequent rise in the proportion of esters in the residue, until the residue comprises 88 per cent. of esters.

My invention is particularly applicable to the acetylation of mixtures of alcohols to produce mixtures well suited as solvents of lacquers made from pyroxylin. A mixture of alcohols from which such a solvent can be made by acetylation is an essential intermediate product in the practice of my invention and a suitable intermediate product is a mixture of primary and secondary normal amyl alcohols and primary and secondary iso-amyl alcohols. I have found that a mixture of amyl alcohols produced by purifying the products of hydrolization of the products of chlorination of pentanes, is a suitable intermediate product for the production of alcohol-ester mixtures in accordance with my invention, such a mixture of alcohols being readily produced by procedure in accordance with my Patents, Nos. 1,691,426, 1,717,136 and 1,717,393, by the practice of which mixtures of alcohols containing substantial proportions of normal alcohols and particularly primary normal alcohols can be produced.

In order to aid in the understanding of my invention, I have shown in the single figure of the drawing hereto annexed, distillation curves of ester-alcohol mixtures having alcohol fractions of different compositions and constituting about 14% of the mixture. The curve B is the distillation curve of an ester-alcohol mixture in which the esters are amyl acetates and the alcohols are lower boiling amyl alcohols of the original mixtures, as in ester-alcohol mixtures produced by esterification of an amyl alcohol mixture in a single step. The initial boiling point is low and the boiling range is low and the final boiling point is relatively low.

In the drawing, the curve A is the distillation curve of a mixture made in accordance with my invention and in which the acetates are amyl acetates and the alcohol fraction, forming about 14% of the mixture, consists mainly of higher boiling alcohol of the original alcohol mixture. It will be observed that the boiling range of the mixture is high and that the initial and final boiling points are high and that the spread between the initial and final boiling points is less than in the case where the alcohol fraction consists of lower boiling alcohols.

Mixtures of alcohols for use in the practice

of my invention can be produced on a commercial scale. A desired hydrocarbon is obtained by distillation or rectification from gasoline produced from natural gas. The desired hydrocarbon or mixture of hydrocarbons may be chlorinated as set forth in my copending Patents No. 1,741,393 issued December 31, 1929, No. 1,835,202 to issue December 8, 1931, and No. 1,717,136 issued June 11, 1929. For example, the hydrocarbon or mixture of hydrocarbons, after vaporization, if necessary, is passed, preferably at a velocity that will produce turbulent flow or a velocity of that order or at least a velocity in excess of one-half of the velocity that will produce turbulent flow, to a reactor heated to a suitable temperature, e. g. about 340° C. in the case of pentane, while chlorine vapor is introduced into the flowing stream of hydrocarbon vapor preferably in a proportion of one part of chlorine to 15 to 20 parts of hydrocarbon vapor, the reactor consisting of an externally heated conduit. The products of chlorination are then properly cooled and passed through a rectifier from which the chlorinated product is withdrawn in liquid form and excess hydrocarbon passing off as a vapor is condensed and a part of it is used as a reflux in the rectifier. Preferably the fresh supply of hydrocarbons and condensed hydrocarbons that are to be passed again through the chlorination step are dehydrated by acidulation, by hydrogen chloride, and removal of precipitated moisture. The chlorinated hydrocarbons may then be hydrolized as set forth in my copending Patents No. 1,691,425 and No. 1,691,426, issued November 13, 1928. Thus the hydrocarbon chloride may be introduced into an iron autoclave together with alkaline salt of a substantially water-insoluble fatty acid, such as oleic, and heated for several hours until the reaction is substantially complete, the temperature being 150° C. in the case of amyl chloride. Then a fresh quantity of hydrocarbon chloride and a fresh quantity of caustic soda solution are added, and the mixture, preferably stirred by external circulation, is heated, for 3 or 4 hours at 150° C. in the case of amyl chloride. The salt water forming in the bottom of the autoclave may be withdrawn and the alcohol may be removed by distilling. The residual oleic ester having the basic radical of the hydrocarbon chloride under treatment is ready to receive a fresh charge of hydrocarbon chloride and caustic soda for a repetition of the process. When amyl chloride made as above-described is hydrolized in this manner the crude product may be purified as described in my copending application, Ser. No. 165,877, filed February 4, 1927, to produce mixtures of amyl alcohols herein referred to. Thus, by rectification, the crude mixture obtained by the hydrolyzing step is dehydrated and the amyl chlorides are dis-

tilled off and then higher boiling chlorides are distilled off with sufficient water present in the kettle of the rectifier to maintain moisture in the distillates at all temperatures up to the boiling point of the lowest boiling desired alcohol. Then the desired mixture of alcohols is distilled off.

While I have described my invention by reference to particular substances and compositions, I do not intend to limit my invention thereto but intend that it shall include such variations and modifications as fall within the hereunto appended claims. In this connection it is to be particularly noted that ester-alcohol mixtures having different alcohol fractions of different composition may be made in accordance with my invention. In this connection the point at which distillation in a rectifying tower is cut in order to achieve substantial removal of all lower boiling alcohols and such esters as pass off therewith is readily determined in connection with any particular mixture of alcohols being esterified in accordance with my invention. In this connection I have found that the cut may be made at a temperature between 125° C. and 130° C., and preferably substantially at 130° C., in acetylating mixtures of amyl alcohol in accordance with my invention.

What I claim and desire to secure by Letters Patent is:

1. In the production of a mixture in commercially desired proportions of alcohols and esters of alcohols, the process comprising esterifying a mixture of aliphatic monohydroxy alcohols of different boiling points to a degree of esterification at which alcohol is present in the product in a proportion higher than that desired in the final product, and separating from the product of esterification by rectification lower-boiling alcohols and such esters as pass off therewith until the residue contains alcohols and esters in the said commercially desired proportions.

2. In the production of a mixture in commercially desired proportions of alcohols and esters of alcohols, the process comprising esterifying a mixture of aliphatic monohydroxy alcohols of different boiling points to a degree of esterification at which alcohol is present in the product in a proportion greater than that desired in the final product, and separating substantially all low-boiling alcohols and some low-boiling esters from the products of esterification by rectification, leaving a residual mixture of esters and higher-boiling alcohols that is substantially free of lower-boiling alcohols of the original mixture.

3. In the production of a mixture in commercially desired proportions of alcohols and esters of alcohols, the process comprising esterifying a mixture of aliphatic monohydroxy alcohols of different boiling points

to a degree of esterification at which alcohols are present in the product in a proportion greater than that desired in the final product, and separating from the products of esterification by rectification a fraction in which the ratio of lower-boiling alcohol to higher-boiling alcohol is greater than in the original alcohol mixture and the ratio of higher-boiling ester to lower-boiling ester is less than the ratio of higher-boiling alcohols to lower-boiling alcohols in the original alcohol mixture, said separation being continued until the alcohols and esters in the residue are in the said commercially desired proportion.

4. In the production of a mixture in commercially desired proportions of alcohols and esters of alcohols, the process comprising esterifying a mixture of aliphatic monohydroxy alcohols of different boiling points to a degree of esterification at which the ratio of alcohol to esters in the product is greater than the said commercially desired proportion, and separating from the products of esterification by rectification a fraction containing lower-boiling alcohols and some lower-boiling esters, leaving a residue in which the ratio of lower-boiling alcohol to higher-boiling alcohol therein is less than in the original alcohol mixture and the ratio of higher-boiling ester to lower-boiling ester therein is greater than the ratio of higher-boiling alcohol to lower-boiling alcohol in the original alcohol mixture.

5. In the production of a mixture in commercially desired proportions of alcohols and esters of alcohols, the process comprising esterifying a mixture of aliphatic monohydroxy alcohols of different boiling points to a degree of esterification at which the ratio of alcohol to esters in the product is greater than the said commercially desired proportion, separating from the products of esterification by rectification lower-boiling alcohol and such esters as pass off therewith until alcohols and esters present are in the commercially desired proportion, adding fresh alcohol aliphatic monohydroxy mixture to the separated fraction, and repeating the process with the resultant mixture.

6. In the production of a mixture in commercially desired proportions of alcohols and esters of alcohols, the process comprising esterifying a mixture of aliphatic monohydroxy alcohols of different boiling points to a degree of esterification at which the ratio of alcohol to esters in the product is greater than the said commercially desired proportion, separating from the products of esterification by rectification lower-boiling alcohol and such esters as pass off therewith until alcohols and esters present are in the said commercially desired proportion, and purifying the residue by distillation.

7. In the production of a mixture in com-

mercially desired proportions of alcohols and acetates of alcohols, the process comprising acetylating a mixture of aliphatic monohydroxy alcohols of different boiling points to a degree of acetylation at which the ratio of alcohols to acetates in the product is greater than the commercially desired proportion, and separating from the products of acetylation by rectification lower-boiling alcohols and such acetates as pass off therewith to produce a residue containing alcohols and acetates in said commercially desired proportion.

8. In the production of a mixture in commercially desired proportions of alcohols and acetates of alcohols, the process comprising acetylating a mixture of aliphatic monohydroxy alcohols of different boiling points to a degree of acetylation at which the ratio of alcohols to acetates in the product is greater than the commercially desired proportion, separating from the products of acetylation by rectification lower-boiling alcohols and such acetates as pass off therewith to produce a residue containing alcohols and esters in commercially desired proportion, adding fresh alcohol mixture to the separated fraction, and repeating the acetylating and rectifying operations with the resultant mixture.

9. In the production of a mixture in commercially desired proportions of amyl alcohols and amyl acetates, the process comprising acetylating a mixture of amyl alcohols to a degree of esterification at which the ratio of alcohol to ester in the product is greater than the commercially desired proportion, and separating from the products of acetylation by rectification lower-boiling amyl alcohols and such amyl acetates as pass off therewith.

10. In the production of a mixture in commercially desired proportions of amyl alcohols and amyl acetates, the process comprising acetylating a mixture of amyl alcohols to a degree of esterification at which the ratio of alcohol to ester in the product is greater than the commercially desired proportion, separating from the products of acetylation by rectification lower-boiling amyl alcohols and such amyl acetates as pass off therewith, and adding a fresh quantity of mixture of amyl alcohols to the separated fraction and repeating the acetylating and rectifying steps with the resultant mixture.

11. In the production of a mixture in commercially desired proportions of amyl alcohols and amyl acetates, the process comprising acetylating a mixture of primary and secondary amyl alcohols to a degree of esterification at which the ratio of alcohol to ester in the product is greater than the commercially desired proportion, and separating from the product of acetylation by rectification lower-boiling amyl alcohols and such acetates as pass off therewith to produce a residue con-

taining primary amyl alcohols and amyl acetates and substantially free of secondary amyl alcohols.

12. In the production of a mixture of alcohols and acetates of alcohols, the process comprising acetylating a mixture of aliphatic monohydroxy alcohols produced by hydrolysis of a mixture of alkyl esters, continuing acetylation to a degree of acetylation at which the ratio of alcohol to ester in the product is greater than that desired in the finished product, and separating from the product of acetylation by rectification lower-boiling alcohols and such acetates as pass off therewith to produce a residue comprising acetates and alcohols and substantially free of lower-boiling alcohols of the original mixture.

13. In the production of a mixture in commercially desired proportions of amyl alcohols and amyl acetates, the process comprising acetylating a mixture of amyl alcohols of different boiling points and containing primary amyl alcohols to a degree of esterification at which the ratio of alcohol to ester in the product is greater than the commercially desired proportion, and separating from the product of acetylation by rectification lower-boiling amyl alcohols and such acetates as pass off therewith to produce a residue containing amyl acetates and higher-boiling amyl alcohols including primary amyl alcohols of the original mixture of alcohols and substantially free of lower-boiling amyl alcohols of the original mixture of alcohols.

14. A composition comprising the distillation residue of the product obtained by subjecting to esterifying treatment a mixture of alcohols of different boiling points, said composition containing esters of the several alcohols and higher-boiling alcohols of said mixture of alcohols and being substantially free of lower-boiling alcohols of said mixture of alcohols.

15. A composition comprising the distillation residue of the product obtained by subjecting to esterifying treatment a mixture of amyl alcohols of different boiling points, said composition containing esters of the several amyl alcohols and higher-boiling amyl alcohols of said mixture and being substantially free of lower boiling amyl alcohols of said mixture.

In testimony whereof, I have signed my name to this specification.

EUGENE E. AYRES, Jr.