This invention relates to the treatment of hydrocarbons in the presence of a particular type of catalyst to produce therefrom products having more desirable properties for motor fuel use or for other specific purposes.

In a broad aspect the present invention relates to the use of a particular type of catalyst for producing hydrocarbons of branched chain structure or hydrocarbons of other more desirable properties such as volatility or octane number from compounds not possessing these properties. More specifically, the process involves the alkylation of a saturated or aromatic hydrocarbon with an olefinic hydrocarbon, or the dealkylation of a high boiling alkyl cyclic hydrocarbon including alkyl napthenic and alkyl aromatic hydrocarbons to produce therefrom a cyclic hydrocarbon having a more desirable boiling point. In a particular application, the present processes may be operated for the specific purpose of producing gasoline range boiling hydrocarbons from other hydrocarbons boiling above or below the desired range. Further, the present process may comprise the isomerization of a saturated hydrocarbon to form a hydrocarbon of more highly branched chain structure, or the autodestructive alklylation of a saturated hydrocarbon to form a product having a wider boiling range than the charged hydrocarbon.

In a typical application, the present invention relates to a process for the production of wider boiling range products by the reaction known as "autodestructive alkylation." In this reaction paraffinic or napthenic hydrocarbons are contacted with a catalytic agent suitable for effecting a substantially simultaneous cracking and alkylation of the hydrocarbons contained in the charge. Thus, a paraffin when reacted under such conditions will form olefin-acting and paraffinic fragments each olefin-acting fragment being capable of reacting with the paraffin fragments so produced or with the original paraffin to yield a variety of condensation products boiling over a wide range and containing a larger number of individual components than the original hydrocarbon charged.

Another typical application of the present invention is in the isomerization of hydrocarbons, usually of saturated or aromatic derivation such as the paraffins, cycloparaffins, or aromatic hydrocarbons, said isomerization comprising an alteration in the carbon structure of the hydrocarbon molecule without changing the molecular weight thereof. The process has particular application in the manufacture of aviation fuels, not only from the standpoint of forming highly branched chain hydrocarbons which in themselves have high antiknock properties from hydrocarbons of straight chain or normal structure, but also in the intermediate preparation of a reactant or reactants involved in a subsequent synthesis, as, for example, the isomerization of n-butane to isobutane for alkylation purposes.

One of the outstanding applications of this invention is in the isomerization of alkylnaphthenes to produce naphthenes containing either fewer or more carbon atoms in the naphthenic ring, depending upon the particular hydrocarbon chosen and the reaction conditions. Thus, methylcyclohexane may be isomerized with the present catalyst under one set of conditions to yield a dimethylcyclopentane, or under another set of conditions to yield ethylcyclopentane. Furthermore, the invention finds application in the isomerization of alkylcyclopentanes to cyclohexane, derivatives which may subsequently be dehydrogenated to yield benzene derivatives. An example of such an operation is the isomerization of methylcyclopentane to cyclohexane, which may be dehydrogenated to benzene. This invention makes possible the synthesis of hydrocarbons which may be otherwise difficult to prepare or to obtain from natural sources.

Still another application of the present invention relates to the dealkylation of hydrocarbons in which an alkyl group is removed from a cyclic hydrocarbon. The present catalyst, hereinafter more fully disclosed, is effective in accomplishing such conversions, but is particularly applicable to dealkylation reactions in which an alkyl group containing 4 or more carbon atoms is to be removed from an aromatic hydrocarbon. It is understood, however, that this invention is not to be limited merely to the treatment of such hydrocarbons but may be extended to any hydrocarbon from which an alkyl group is removable.

It is one object of this invention to react an olefinic hydrocarbon with a hydrocarbon condensable therewith in the presence of a particular catalyst to form a hydrocarbon having a higher boiling point and a more highly branched structure.

Another object of this invention comprises isomerizing a paraffinic, naphthenic, or aromatic hydrocarbon in the presence of the novel catalyst hereinafter described.

A further object of this invention is to provide a process for the autodestructive alkylation of a paraffinic or a naphthenic hydrocarbon to form...
a product having a wider boiling range than the hydrocarbon initially charged.

It is still another object of this invention to prepare catalysts useful in hydrocarbon alkylation, dealkylation, isomerization, and autodestructive alkylation reactions by forming a complex addition product of an aluminum halide and an unsaturated ketone. In one embodiment the present invention relates to a hydrocarbon conversion process which comprises reacting a hydrocarbon at conversion conditions in the presence of a catalyst formed by interacting at least one but no more than three molecule proportions of an aluminum halide selected from the group comprising aluminum chloride and aluminum bromide with a molecular proportion of an olefinic ketone.

In one specific embodiment the present invention relates to a process for producing branched chain hydrocarbons of higher molecular weight charge than the hydrocarbon initially charged. It is still another object of this invention to prepare catalysts useful in hydrocarbon alkylation, dealkylation, isomerization, and autodestructive alkylation reactions by forming a complex addition product of an aluminum halide and an unsaturated ketone. In one embodiment the present invention relates to a hydrocarbon conversion process which comprises reacting a hydrocarbon having a lesser degree of branching at a temperature within the range of about 100° C. to 100° C. In the presence of a catalyst formed by interacting at least one but no more than three molecule proportions of an aluminum halide selected from the group comprising aluminum bromide and aluminum chloride with an olefinic ketone.

Other embodiments of the present invention will become apparent in considering the specifications hereinafter discussed.

I have found that catalysts useful in isomerization, various types of alkylation reactions, including autodestructive alkylation, and dealkylation may be prepared by reacting an olefinic ketone with an aluminum halide of the middle halogens (that is aluminum chloride and aluminum bromide) to form a complex addition product thereof. Especially active catalysts comprising the said addition products have been prepared containing a 1:1 molar ratio of aluminum halide and olefinic ketone, indeed act catalytically in the present processes, but acquire the characteristics of the unmodified aluminum halides as the molecular proportion of halide to ketone in the catalyst increases beyond a 3:1 ratio. In contrast to the unmodified aluminum halide catalysts, including aluminum chloride and aluminum bromide, the catalysts of the present invention do not form substantial amounts of sludge-like materials with unsaturated and aromatic hydrocarbons. Accordingly, the metal halide-olefinic ketone may be used as catalysts in continuous processes over long periods of time with relatively little contamination so that the catalyst life is substantially longer than the life of the corresponding aluminum halide itself in similar types of hydrocarbon conversion reactions. Another advantage of the composite catalyst of the present invention is its ability to catalyze the alkylation of an isoparaffin with an olefin without causing any substantial formation of low boiling and relatively complex alkylation products similar to those observed when cracking occurs in the presence of aluminum chloride.

The olefinic ketone utilisable in preparing the aluminum halide-ketone catalysts of this invention may be selected from the relatively large number of compounds represented by the class referred to as olefinic ketones. Typical examples of these ketones include mesityl oxide (isopropylidenedieneacetone), phenone (dipropylidenedieneacetone), methylvinyl ketone, ethylvinyl ketone, divinyl ketone, ethylidenedieneacetone, allylacetone, etc. In general, however, the low molecular weight ketones, containing up to about 10 carbon atoms per molecule are usually preferred, since olefinic ketones of low molecular weight generally form aluminum halide-ketones which are liquid at the operating conditions employed in the present processes. Liquid catalysts of the present type are usually preferred since more intimate contact of the catalyst with the hydrocarbons may be obtained with a liquid catalyst especially when utilizing mixing devices in the reactors employed in the process. A particularly desirable ketone for the preparation of the catalysts of the present type is mesityl oxide, which yields an addition product with aluminum chloride or aluminum bromide, which is liquid at the operating conditions commonly employed in these processes.

The olefinic ketones of this invention may be selected from a broad range of suitable ketones, such as for example, the condensation of acetone to yield pherone or mesityl oxide. The ketone may also be conveniently prepared by the isomerization of an aldehyde, such as the isomerization of crotonaldehyde to yield methylvinyl ketone.

In thus specifying the preferred liquid aluminum halide-ketones, it is not intended to limit the scope of the present invention strictly to the liquid addition products, because in some instances may be preferable to employ under certain modified conditions of operation a solid ketonate, as for example, in a vapor or gaseous phase conversion reaction where a fixed bed of solid catalyst is maintained within the reactor and the reactants pass over the catalyst in gaseous state. Furthermore, the unsaturated aluminum halide-ketone may be mixed with or deposited on carrying or spacing materials of a relatively inert character such as various prepared forms of alumina, silicas, activated carbons or chars, synthetic composites, and acid-treated clays, such as acid-treated montmorillonite. The preferred catalytic composites may be prepared in the presence of these carriers in relatively finely divided condition so that an intimate mixture of catalyst and carrier is produced, which may be formed into particles by pelleting or extrusion procedures, or they may be prepared separately and used to surface prepared granules.

The hydrocarbons utilisable as starting materials for the various processes of the present invention comprises paraffinic, olefinic, naphthenic, and aromatic hydrocarbons, the particular hydrocarbon or hydrocarbons to be treated in the reaction depending upon the specific conversion and products desired. The paraffins and olefins include both normal and isomeric forms, while the naphthenes and aromatics comprise cyclic hydrocarbons or their alkyl derivatives. The various types of hydrocarbons which may be converted by the present catalyst into branched chain hydrocarbons and into a lower or higher boiling product than the initial charge stock are hereinafter referred to more specifically in connection with the reactions under consideration.

Isobutane is the isoparaffin commonly subjected to alkylation, although higher molecular
weight isoparaffins also react with olefinic hydrocarbons under similar or modified conditions of operation to produce branched chain paraffinic hydrocarbons of higher boiling point than the isoparaffinic hydrocarbons charged to the process. However, the isoparaffins, such as isopentane, isohexane, etc., are themselves valuable constituents of gasoline, they are consequently used less commonly than iso- butane as charging stocks for the alkylation process.

Of the various naphthenic hydrocarbons which may be alkylated in the presence of the catalyst of the type herein described to produce naphthenic hydrocarbons of more highly branched chain structures cyclohexane or its alkyl derivatives is commonly employed in such alkylation; however, cyclopentane and cycloheptane or their alkyl derivatives may also be utilized to advantage. The resulting alkylates are utilizable as constituents for high anti-knock gasoline. Aromatic hydrocarbons such as benzene, toluene and other alkyl benzenes, napthalenes and other aromatic hydrocarbons, which are alkylatable by olefinic hydrocarbons as heretofore set forth, may be obtained from any source, such sources being well known to those familiar with the art. Alkyl aromatic hydrocarbons herein referred to include both mono-alkyl and poly-alkyl aromatic hydrocarbons which may be converted into more highly alkylated aromatic hydrocarbons.

Olefif hydrocarbons utilizable in the present alkylation process comprise mono-olefins having one double bond per molecule and poly-olefins having more than one double bond per molecule. Mono-olefins which may be utilized for alkylation of paraaffinic, naphthenic, or aromatic hydrocarbons, phenols, or aromatic amines in the presence of the catalyst herein described are either normally gaseous or normally liquid and include ethylene, propylene, butylene, amylene and higher normally liquid olefins, the latter including various polymers of gaseous olefins. Cyclic olefins, such as cyclohexene, may also be utilized, but generally not under the same conditions of operation applying to the non-cyclic olefins. The polyolefinic hydrocarbons utilizable in the present process include conjugated diolefins, such as butadiene and isoprene, as well as non-conjugated diolefins and other polyolefinic hydrocarbons containing more than two double bonds per molecule.

Alkylation of the above alkylatable hydrocarbons may also be effected in the presence of the hereinabove referred to catalyst by reacting said hydrocarbons with certain substances capable of producing olefinic hydrocarbons under the conditions of operation chosen for the process. Such olefin-producing substances include alkyl halides capable of undergoing dehydrohalogenation to form olefinic hydrocarbons containing at least two carbon atoms per molecule. The alkylhalides comprise a particularly desirable group of compounds which act as olefin producers in admixture with alkylatable hydrocarbons and catalyst of the present type, since in the reaction, hydrogen halide is also produced which acts as a desirable catalytic promoter in the reaction. In each case the olefinic hydrocarbons and the above-men- tioned olefin-producing substances are herein referred to as olefin-acting compounds.

In accordance with the process of the present invention the alkylation of a naphthenic, paraaffinic, or aromatic hydrocarbon with an olefin-
by the nature of the reactants and by the composition of the catalyst used in the process.

The operating conditions maintained for a dealkylation reaction are usually more severe than in the alkylation process. Conversion temperatures may vary from about 10° to about 150° C, and pressures up to about 10 to 20 atmospheres are usually maintained during the reaction, although other temperature and pressure conditions may be used in some instances. Generally speaking, the upper temperature limit is determined in the case of dealkylation reactions by the instability of the catalyst at temperatures substantially greater than 150° C, rather than by any temperature requirement to effect the conversion. Dealkylation reactions may be conducted on paraflinic, alkynaphthenic, or alkylaromatic hydrocarbons, but is especially applicable to alkylnaphthenic hydrocarbons for the removal of an alkyl group from a benzene or condensed-ring aromatic derivative. A typical example of such an operation is exemplified by the removal of a tertiary butyl group from the corresponding alkylnaphthene derivative to produce benzene as a major product of the reaction. Dealkylation reactions are further applicable to the removal of other more side chains from a polyalkylated aromatic hydrocarbon, such as para-tertiary butyltoluene which may be dealkylated under a given set of conditions to yield toluene, or under more severe conditions to yield benzene.

Saturated hydrocarbons, which may comprise paraffins or naphthenes, are usually the class of hydrocarbons treated in autodestructive alkylation reactions. The paraffins are generally of at least C\textsubscript{1} molecular weight or higher and of branched or straight chain. The naphthenes may be highly substituted with alkyl groups of either normal or straight chain configuration. Temperatures of from about 0° to about 150° C, and superatmospheric pressures up to about 70 to 80 atmospheres are usually maintained to effect autodestructive alkylation. The conversion conditions are primarily dependent upon the character of the products desired, the higher temperatures generally causing the formation of short chain hydrocarbons and lower temperatures usually favoring the formation of higher molecular weight products. As indicated previously, the product will boil over a much broader range than the hydrocarbons initially charged.

In the normal isomerization and autodestructive alkylation reactions as effected under the reaction conditions herein specified, isomerization, with substantially no accompanying autodestructive alkylation may be obtained by adding to the reaction mixture a modifying constituent, such as hydrogen, or a hydrocarbon diluent which tends to suppress autodestructive alkylation and to enhance the isomerization of the reactants. The addition of a modifying constituent may also be accompanied by a change in the reaction conditions.

In converting paraflinic or naphthenic hydrocarbons to effect isomerization or autodestructive alkylation thereof, or in the dealkylation of a naphthenic or aromatic hydrocarbon with the type of catalysts herein described, either batch or continuous operations may be employed. In a simple batch procedure a proportioned amount of a paraflinic hydrocarbon, for example, catalyst and an equivalent amount of hydrogen halide may be added to a vessel capable of withstand ing moderately superatmospheric pressure and the contents heated for a time adequate to cause the desired degree of conversion. In some instances, especially when normally liquid paraflinic hydrocarbons are treated, undesirable decomposition reactions may be minimized by introducing hydrogen into the reactor in contact with the reactants charged therein. After a period of heating, the reaction vessel may be cooled, the gaseous contents of the liquid hydrocarbon layer separated from the partially spent catalyst, and fractionated to recover desired products and insuflciently converted hydrocarbons, the latter being suitable for returning for further treatment.

In continuous operations the granular catalyst, either alone or on carriers, may be placed in the reaction chamber, through which preheated mixtures of hydrocarbon along with hydrogen halide may be passed. In liquid catalyst systems, the hydrocarbons may be added as liquids and the mixture stirred to effect contact of the hydrocarbons and catalyst or the hydrocarbons may be vaporized and passed into a pool of the catalyst. Hydrogen admixed with the hydrocarbons may also be used in such operations if it is found that greater selectivity in the formation of desired compounds is obtained thereby. The products obtained in such treatments may be continuously fractionated to separate light gases, hydrogen halide, reaction products, and insufficiently converted hydrocarbons, the hydrogen halide and unconverted hydrocarbons being recycled to the reaction zone for further treatment, while the desirable reaction products are recovered.

The alkylation of a saturated or aromatic hydrocarbon by an olefinic hydrocarbon or other olefin-acting compounds may be carried out using either batch or continuous operation. In batch types of operation, a liquid or finely divided catalyst formed by interacting an aluminum halide and an unsaturated ketone is charged to a reactor containing a saturated or aromatic hydrocarbon such as an isoparaffin or benzene, and the resultant mixture is then agitated, while an olefinic fraction, or a hydrocarbon fraction containing both olefin and alkylatable hydrocarbons is added thereto in order to effect the desired condensation of the olefin and the alkylatable hydrocarbons. After reaction, the hydrocarbon layer is separated from the catalyst and the former is then fractionally distilled into unconverted hydrocarbon and alkylation products. The unconverted hydrocarbon and unconverted catalyst may then be employed in another alkylation run.

Continuous types of alkylation treatment may be carried out by introducing a mixture of alkylatable saturated or aromatic hydrocarbons and an olefin into a reaction containing a fixed bed of granular catalytic material, formed for example, by interacting substantially anhydrous aluminum chloride with an unsaturated ketone such as phorone or a high molecular weight ketone as hereinabove described. The olefin charged to the alkylation reactor may thus be introduced with an alkylatable hydrocarbon or it may be directed to contact with said saturated or aromatic hydrocarbon at a number of points intermediate the inlet and outlet points of the alkylation zone. The conditions of temperature and pressure maintained in such an alkylation zone are generally between the approximate limits set forth above, but the exact conditions employed in any particular alkylation generally vary with the molecular weights and reactivities of the sat-
urated and olefinic hydrocarbons reacting, the composition of the catalyst, and other factors. It is generally advantageous to dilute olefinic hydrocarbon or olefin-acting compounds with a portion of the saturated hydrocarbon and to introduce the olefin-containing mixture at a plurality of points throughout the reaction zone, rather than to add the diluted olefinic hydrocarbons directly to the alkylation zone. In this way a relatively high ratio of saturated hydrocarbons to olefinic hydrocarbons is readily maintained throughout the entire reaction zone so that alkylation is thereby favored and polymerization of the olefin is kept at a low level. The recovered mixture obtained from a continuous distillation is then conducted to a separating or fractionating zone in which unconverted alkylatable hydrocarbons are separated from the alkylation product, said unconverted hydrocarbons being recycled to further treatment in the alkylation zone of the process.

As hereinabove noted, organic compounds other than hydrocarbons may be subjected to alkylation or dealkylation to effect either the introduction or removal of an alkyl group to or from the aromatic nucleus, depending upon the reaction desired. Organic compounds other than those of purely hydrocarbon nature, which may be alkylated or dealkylated with the present catalyst, include, in general, the hydroxybenzenes and the hydroxybenzenes methylated, bis(methylated), and the aromatic amines, such as aniline or its alkyl derivatives (for example, toluidine, etc.).

The following examples are given to illustrate the character of results obtained by the use of the present process and catalysts, although the procedures presented is not introduced with the intention of unduly restricting the generally broad scope of the invention.

**Example I**

2.2 mols of n-pentane (144 g.) was stirred at 10 to 25° C. with a mixture of 5 mols (49 g.) of mesityl oxide and 0.67 mol (90 g.) of aluminum chloride. The mixture was stirred for 2 hours at the temperature followed by separation of the catalyst from the hydrocarbon layer by decantation. The yield of hydrocarbons obtained, which amounted to 89 percent based on the n-pentane charged, consisted of 12 percent isobutane, 11.5 percent isopentane, 61.5 percent n-pentane, and an 8 percent yield of CH₄ and C₂H₆.

An autodestructive alkylation reaction conducted on n-pentane using the same reaction conditions as specified above, but conducted in the presence of pure aluminum chloride, promoted by hydrogen chloride, resulted in no conversion of the n-pentane. The hydrocarbon was recovered unchanged.

**Example II**

The high activity of the mesityl oxide-aluminum chloride complex was shown by the behavior of isopentane for this reaction. The reaction was conducted under similar experimental conditions as n-pentane in Example I above. The yield of hydrocarbon layer recovered was 89 percent based on isopentane charged; 63 percent of the recovered hydrocarbons distilled below 50° C., and were composed of 35 percent isobutane, 55 percent isopentane, and 7 percent n-pentane. The higher-boiling hydrocarbons contained about 30 percent of hexanes composed predominantly of 2,3-dimethylbutane and of 2-and 3-methylpentane. The heptane fraction was composed of 2,3-dimethylpentane and of 2- and 3-methylhexane.

**Example III**

40 g. (0.3 mol) of anhydrous aluminum chloride and 30 g. (0.306 mol) of mesityl oxide are cooled separately to −78° C. and are then mixed in a glass reactor surrounded by a cooling bath. A rapid reaction ensues on stirring the catalytic components and a lumpy mass of solid reaction product forms.

35 g. of benzene, 15 g. of tertiary butyl chloride, and 20 g. of the catalyst as prepared above are mixed in a glass reactor and allowed to set at 25° C. with occasional shaking for a period of 2 hours. The reaction product formed in this condensation contains 40 g. of liquid which upon washing, drying, and distilling is found to contain 8 g. of tertiary butylbenzene and 8.5 g. of higher boiling alkylbenzenes consisting mainly of p-dl-tertiary butylbenzene.

I claim as my invention:

1. A hydrocarbon conversion process which comprises reacting a hydrocarbon at conversion conditions in the presence of a catalyst formed by interacting at least 1, but not more than 3 molecular proportions of an aluminum halide selected from the group consisting of aluminum chloride and aluminum bromide with an olefinic ketone.

2. A process for producing branched chain hydrocarbons from hydrocarbons of less highly branched chain structures which comprises reacting said hydrocarbon material in the presence of a catalyst formed by interacting at least 1, but not more than 3 molecular proportions of an aluminum halide selected from the group consisting of aluminum bromide and aluminum chloride with an olefinic ketone.

3. A process for alkylation of an alkylatable hydrocarbon which comprises contacting said alkylatable hydrocarbon with an olefin-acting compound in the presence of a catalyst formed by interacting at least 1, but not more than 3 molecular proportions of an aluminum halide selected from the group consisting of aluminum bromide and aluminum chloride with an olefinic ketone.

4. A process for alkylation of an aromatic hydrocarbon with an olefinic hydrocarbon which comprises contacting said aromatic hydrocarbon with said olefinic hydrocarbon in the presence of a catalyst formed by interacting at least 1, but not more than 3 molecular proportions of an aluminum halide selected from the group consisting of aluminum bromide and aluminum chloride with an olefinic ketone.

5. A process for alkylation of a paraffinic hydrocarbon with an olefinic hydrocarbon which comprises contacting said paraffinic hydrocarbon with said olefinic hydrocarbon in the presence of a catalyst formed by interacting at least 1, but not more than 3 molecular proportions of an aluminum halide selected from the group consisting of aluminum bromide and aluminum chloride with an olefinic ketone.

6. The process of claim 5 further characterized in that said paraffinic hydrocarbon is isobutane and said olefinic hydrocarbon is a butylene.
not more than 3 molecular proportions of an aluminum halide selected from the group consisting of aluminum bromide and aluminum chloride with an olefinic ketone.

8. A process for the isomerization of a polyalkylated naphthenic hydrocarbon which comprises contacting said naphthenic hydrocarbon with a catalyst formed by interacting at least 1 but not more than 3 molecular proportions of an aluminum halide selected from the group consisting of aluminum bromide and aluminum chloride with an olefinic ketone.

9. A process for isomerizing a polyalkylated aromatic hydrocarbon which comprises contacting said aromatic hydrocarbon with a catalyst formed by interacting at least 1 but not more than 3 molecular proportions of an aluminum halide selected from the group consisting of aluminum bromide and aluminum chloride with an olefinic ketone.

10. A process for the autodestructive alkylation of a paraffinic hydrocarbon which comprises contacting said paraffinic hydrocarbon with a catalyst formed by interacting at least 1 but not more than 3 molecular proportions of an aluminum halide selected from the group consisting of aluminum bromide and aluminum chloride with an olefinic ketone.

11. The process of claim 10 further characterized in that said catalyst comprises a reaction product of at least 1 molecular proportion of an aluminum halide with 1 molecular proportion of mesityl oxide, the process being conducted at a temperature within the range of from about 0° to about 150° C., and at a superatmospheric pressure up to about 70 to about 80 atmospheres.

12. In the art of effecting hydrocarbon reactions which are catalyzed by aluminum halide catalysts, the improvement which comprises carrying out the reaction in the presence of the addition product of an olefinic ketone and from 1 to 3 molecular proportions of an aluminum halide selected from the group consisting of aluminum chloride and aluminum bromide.

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REFERENCES CITED

The following references are of record in the file of this patent:

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<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
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<tbody>
<tr>
<td>2,076,301</td>
<td>Langedijk et al.</td>
<td>Apr. 6, 1937</td>
</tr>
<tr>
<td>2,368,853</td>
<td>Francis</td>
<td>Feb. 6, 1945</td>
</tr>
<tr>
<td>2,389,266</td>
<td>Francis et al.</td>
<td>Nov. 20, 1945</td>
</tr>
</tbody>
</table>