

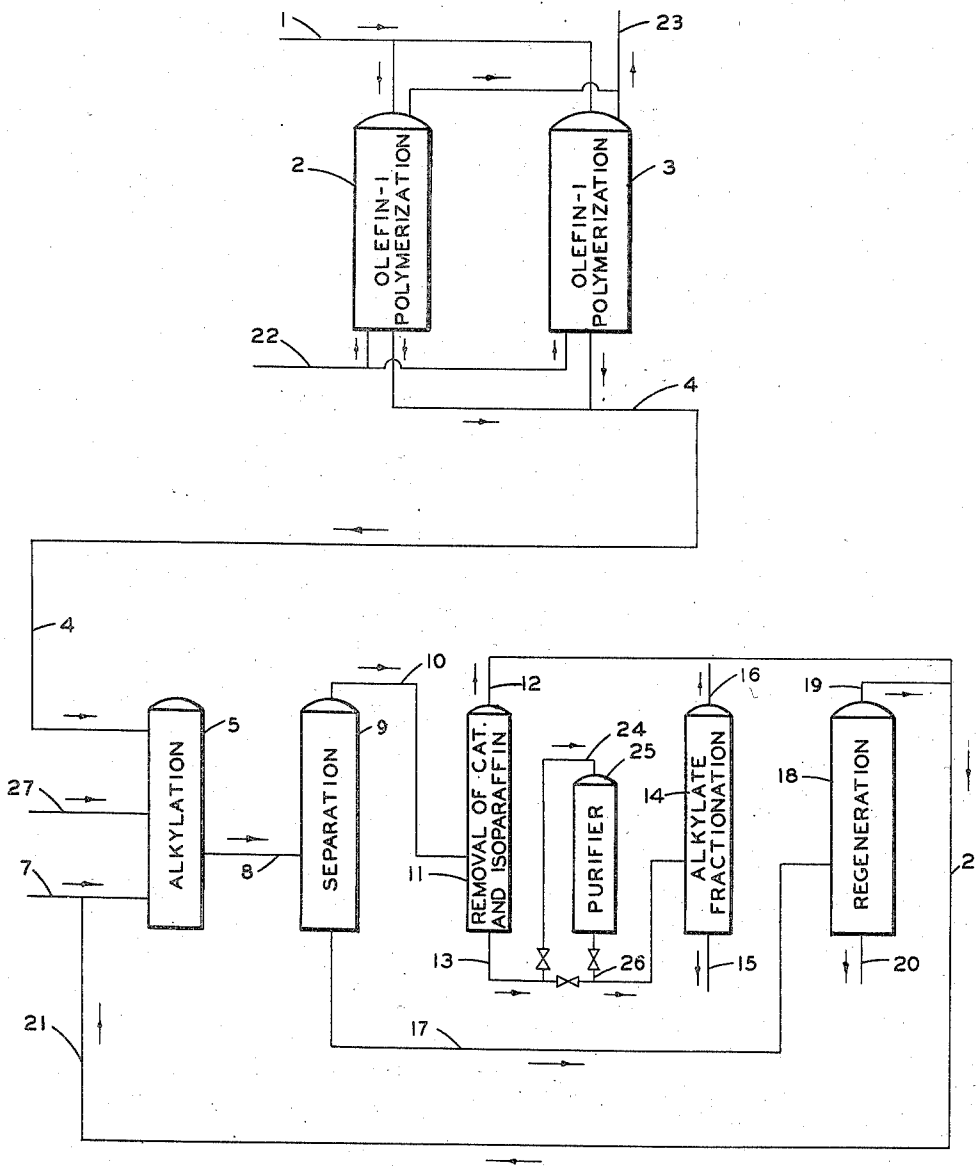
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POLYMERIZATION AND ALKYLATION OF HYDROCARBONS

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POLYMERIZATION AND ALKYLATION OF
HYDROCARBONS

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This invention relates to the production of motor fuels. In one aspect it relates to the preparation of a feed stock for use in the production of high octane-number motor fuels. In another aspect it relates to the production of high octane number motor fuels or blending stocks therefor, in high yields.

One specific embodiment of my invention involves treatment of a feed stock containing one or more 1-olefins, one or more 2-olefins and one or more isoparaffins for removal of the 1-olefins and exposing the resulting hydrocarbon mixture to alkylation conditions in the presence of, for example, hydrofluoric acid, to produce a high yield of alkylate based on the olefin content of the alkylation feed. The process is especially applicable to olefins and isoparaffins of 3 to 5 carbon atoms per molecule. Specifically, my invention involves treatment of petroleum refinery streams containing predominantly low molecular weight 1-olefins, 2-olefins and isoparaffins, for example those of 3 to 5 carbon atoms, for removal of the 1-olefins and producing alkylate from the 1-olefin depleted material.

One object of my invention is to provide a process for producing high anti-knock motor fuel or blending stocks therefor.

Another object of my invention is to provide a process for producing high anti-knock alkylate in high yield based on the olefin content of the feed stock to the alkylation reaction.

Still another object of my invention is to provide a process for producing high anti-knock alkylate suitable for blending in motor fuels from available plant streams containing olefin and isoparaffin hydrocarbons and too volatile for automotive fuel use.

Yet another object is to provide a process for removing 1-olefins from such feed streams prior to the alkylation step and in such a form as to be commercially useful.

Other objects and advantages of my process will be realized upon reading the following disclosure.

The drawing illustrates diagrammatically one arrangement of apparatus for practicing the method of my invention.

One specific embodiment of the present invention comprises selective polymerization of 1-olefins in a mixture of olefins including, for example, propylene, 1-butene and 1-pentene and thereafter catalytically alkylating a low-boiling isoparaffin such as isobutane and/or isopentane with the remaining 2-olefin and/or isoolefin, preferably in the presence of a catalyst comprising hydrogen fluoride. By this operation, paraffins for use in motor fuels are obtained which are superior in quality to those obtainable by alkylation of the isoparaffins with an original 1-olefin and 2-olefin containing feed stock. As is well known, high-octane motor fuel can be produced by the alkylation of low-boiling isoparaffins with low-boiling olefins in the presence of suitable catalysts whereby the isoparaffins condense with the olefins to form saturated compounds within the gasoline boiling range. While

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various isoparaffins and olefins can be employed for this alkylation reaction, those containing 4 carbon atoms to the molecule are especially desirable not only because they produce alkylation products having highly desirable octane ratings but also because they are readily available in large quantities. Charge stocks for the production of alkylate motor fuel comprising butane-butene mixtures are obtained for example, by dehydrogenation of butane fractions separated from natural gas, by fractionation of cracking-still gases, or from other refinery streams. These charge stocks may contain all the butane and butene isomers, especially isobutane, normal butane, isobutene, butene-1 and butene-2 in varying, although significant proportions. The nature of the butene isomer subjected to the alkylation reaction affects the yield and quality of the product. Isobutene and butene-2 give alkylate products superior in yield and quality to alkylates from isobutene and butene-1 mixtures.

It has been found that certain chromium oxide catalysts (subsequently described herein) selectively catalyze the polymerization of 1-olefins to high polymers. By "high polymers," I mean polymers having a molecular weight of the order of 500 or higher, usually 1000 and higher, e. g. in the range 1000 to 200,000 and greater. The 1-olefins ordinarily involved here are those having from 3 to 8 carbon atoms per molecule and include propylene, 1-butene, 1-pentene, 1-hexene, 2-methyl-1-pentene, 1-heptene, and 1-octene. The 1-olefin must have no branching nearer the double bond than the 4-position unless it is a conjugated diolefin, in which case branching at the 3-position is permissible. The catalyst promotes the polymerization of other olefins, such as 2-butene, 2-pentene, isobutene, 2-hexene, 3-hexene, and the like, but the products are ordinarily relatively low-boiling liquids, such as the dimer, the trimer, and the like. Also the yield of polymer from the 1-olefins is generally much greater than from the unbranched olefins which have no terminal double bond.

The chromium oxide catalyst utilized for the 1-olefin polymerization comprises chromium oxide associated with at least one additional oxide selected from the group consisting of silica, alumina, zirconia, and thoria. The additional oxide is often used in a highly porous form, such as a gel. It is desirable, in order to obtain maximum activity, that an appreciable portion of the chromium in the chromium oxide be present in the hexavalent state and that the catalyst be activated by heating at an elevated temperature, preferably under non-reducing conditions or in a nonreducing atmosphere. The total chromium content of the catalyst can range from 0.1 to 50 weight percent or higher, but is most frequently in the range 0.1 to 30 weight percent, e. g. from 1 to 5 weight percent. The hexavalent chromium content of the catalyst, as determined by leaching with water and determining the chromium content of the leachings, is at least 0.1 weight percent. Although the catalyst can be prepared by a variety of methods, a highly suitable method comprises impregnating at least one of said additional oxides with an aqueous solution of a chromium salt ignitable to chromium oxide, draining away excess solution, drying, and heating or calcining at a temperature in the range 450 to 1500° F., preferably 750 to 1100° F. The calcination or heating is preferably conducted in a non-reducing atmosphere, preferably in the presence of oxygen, and in the absence of water. Air having a dew point of 0° F. and lower is highly satisfactory as an atmosphere for the calcination.

The polymer of the 1-olefin can be fractionated to obtain fractions which are useful as adhesives for surgical and pressure sensitive tapes, as constituents of calking and sealing compounds, as adhesives for the manufacture

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of laminated paper, as hydraulic fluids, as coatings for tracing paper and for electrical capacitors, other surface coatings and rubber extenders. Some of the polymer products can be used as lubricating oils or additives therefor.

A suitable chromium oxide-silica-alumina catalyst can be prepared by impregnation of a silica-alumina composite with a solution of a chromium compound followed by drying and activation at about 930° F. in a stream of dry, oxygen-containing gas for 5 hours. The catalyst can be prepared by using chromium oxide (preferably the trioxide), chromic nitrate, chromic chloride, chromic sulfate, or chromic acetate. The highest conversions are obtained from catalysts that contain chromium only in the form of oxide after activation. Impregnation with chromium trioxide is preferred, although chromium trinitrate can be used. It is believed that the catalysts prepared from the chloride and sulfate are partially converted to oxide during activation. The concentration of chromium in the catalyst can range from 0.1 to 30 weight percent, but is usually in the range of 1 to 25 weight percent and often in the range 0.1 to 10 weight percent. The catalyst support may be alumina and/or silica. A composite catalyst support containing a major portion of silica and a minor portion of alumina is highly satisfactory. A commercial 90 weight percent silica-10 weight percent alumina coprecipitated gel often used as a cracking catalyst has been used as a support for chromium oxide, the resulting catalyst being highly active for the 1-olefin polymerization. This silica-alumina, having been treated with steam-air mixture at elevated temperatures (500-1000° F.), is macroporous. This property is believed important in the removal of the heavy polymer from the chromium oxide-silica alumina catalyst surface. A chromium oxide-silica catalyst tends to become deactivated more readily than a chromium oxide-silica-alumina catalyst. A chromium oxide-alumina catalyst usually has a lower activity than a chromium oxide-silica-alumina catalyst. The reaction can be carried out by fixed-bed or mobile catalyst technics.

Although the selective polymerization according to this invention can be conducted over a broad range of conditions, the preferred conditions for the polymerization using chromium oxide-silica-alumina catalyst include a temperature in the range of 150 to 250° F., more preferably 170-225° F., a pressure sufficient to maintain the hydrocarbon mixture substantially in the liquid phase, and a reaction time from 15 minutes to 20 hours.

A refinery C₃-C₄ stream can be charged at polymerization conditions using chromium oxide-silica-alumina catalyst to produce tacky polymer and an improved alkylate feed stock in accordance with this invention. Propylene and 1-butene are converted to tacky polymer. 2-butene does not react appreciably, and isobutene is converted to dimer and trimer which still react to give high quality alkylate. Alkylate quality is thus improved while the 1-butene is selectively removed and converted to a more valuable product. The invention includes a combination of steps which comprises selectively polymerizing one or more straight-chain 1-olefins in a mixture of one or more other olefins, as by contacting under suitable polymerization conditions with a catalyst like chromium oxide-silica-alumina that selectively polymerizes the unbranched 1-olefins, removing the resulting polymer, and utilizing the resulting 1-olefin-depleted mixture for alkylation, as in hydrofluoric acid alkylation of an isoparaffin. The alkylation reaction of the process is the known alkylation reaction carried out in the presence of hydrofluoric acid catalyst, such as is described and exemplified in my Patent 2,502,015 (1950).

Individual olefins were polymerized in runs utilizing a fixed bed of chromium oxide-silica-alumina catalyst (Cr content 4 weight percent) at a pressure of 600 pounds per square inch at 190° F. and 2 liquid hourly

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space velocity of feed containing 20 mol percent of the olefin and 80 mol percent isobutane. The duration of the runs was 4 to 6 hours; resulting conversions and the qualitative nature of the polymers were as follows:

Monomer	Average Conversion, percent	Type of polymer, etc.
Normal 1-olefins:		
Propylene.....	91	tacky, semi-solid.
1-Butene.....	75	tacky, elastic semi-solid.
1-Pentene.....	82	tackier than polypropylene; semi-solid.
Normal 2-olefins:		
2-butene.....	5	liquid (dimer and trimer).
2-pentene.....	5	liquid.
Branched 1-olefins:		
Isobutylene.....	87	liquid (dimer and trimer).
2-methyl-1-butene.....	6	liquid.

The catalyst was prepared by impregnating 90 weight percent silica-10 weight percent alumina coprecipitated gel composite with a 1-molar aqueous solution of chromium trioxide, drying the impregnated solid and heating in dry air at 930° F. for 5 hours.

These results illustrate the nature of the polymerization and show that 1-olefins form tacky, semi-solid polymer with the chromium oxide-silica-alumina catalyst, and can thereby be removed from the other olefins. The 2-olefins react to a relatively slight degree, while the branched olefins such as isobutylene are converted to dimer and trimer which still react to give high quality alkylate. Alkylate quality is thus improved while the 1-olefins are selectively removed and converted to a more valuable product.

The improvement in alkylate quality and yield is illustrated by the following data:

Olefin	Isoparaffin	Aviation Range Alkylate Fraction			
		Cut Point, ° F.	Yield, percent	Oct. No.	1 cc. TEL
Butene-1.....	Isobutane.....	356	91.4	89.2	-----
Butene-2.....	do.....	365	97.9	92.7	-----
Pentene-1.....	do.....	320	86.4	83.8	93.0
Pentene-2.....	do.....	347	97.0	89.2	100.4
Butene-1.....	Isopentane.....	284	80.7	74.6	87.7
Butene-2.....	do.....	293	84.3	79.2	89.3

In the operation of my process, as illustrated in the accompanying drawing, catalyst chambers 2 and 3 are charged with the above described chromium oxide-silica-alumina catalyst. The 1-olefin, 2-olefin and isoparaffin charge stock is passed through line 1 from a source, not shown, into for example, reactor 2. The catalyst is maintained at a temperature between about 170° and 225° F. The 1-olefin hydrocarbon or hydrocarbons polymerize in the presence of the catalyst to a tacky semisolid material which is retained on the catalyst. The 1-olefin hydrocarbon depleted stock leaves the bottom of vessel 2 and is transferred via line 4 to an alkylation vessel 5. In this vessel the charge stock containing mainly 2-olefin and isoparaffin hydrocarbons is contacted with, for example, hydrogen fluoride under alkylating conditions. The reaction products are passed through line 8 into a separation zone 9 in which hydrocarbon and acid layers are allowed to separate, the hydrocarbon layer being above the acid layer. The separated hydrocarbon layer is withdrawn via line 10 and introduced into a fractional distillation column 11 for separation of accompanying hydrogen fluoride catalyst and unalkylated isoparaffin hydrocarbons. These latter materials pass overhead from this still via lines 12 and 21 and are recycled into the alkylation zone 5. Bottoms from the still 11 are passed via line 13 into an alkylate fractionator 14 in which high antiknock motor fuel is

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separated from high boiling material. The motor fuel is passed through line 16 to storage or such disposal as desired. Bottoms from column 14, usually small in quantity, are removed via line 15 for such disposal as desired.

Since the alkylate contains organically combined fluorine, usually about 0.01 weight percent, it is preferably passed through line 24 into a purifier zone 25 containing a metal impregnated contact material or bauxite at a temperature of about 200° to 500° F. These materials effect the removal of organic fluorine compounds. Alkylate substantially free from organic fluorine is then passed from the purifier 25 through line 26 into the line 13 for passage into the alkylate still in which the alkylate is fractionated as above stated.

The acid layer in the separation zone 9 is withdrawn therefrom through a conduit 17 and introduced into a hydrofluoric acid regeneration zone 18. When hydrofluoric acid is used as the alkylation catalyst zone 18 can be a still in which the acid, together with any unreacted isoparaffin hydrocarbon is removed overhead via line 19. From this line the catalyst is passed on through lines 21 and 7 into the alkylation zone 5. An organic residue, which is usually small in volume, is withdrawn through line 20 for such disposal as desired. Makeup catalyst, as needed, can be added to the system through line 7.

When sufficient tacky polymer accumulates in reactor 2 to restrict hydrocarbon flow therethrough, the charge stock can be switched from reactor 2 to reactor 3. The polymer is then removed from reactor 2 by backwashing with such a hydrocarbon solvent as propane, isobutane, n-pentane, isopentane, n-heptane, isooctane, cyclopentane, cyclohexane, benzene, toluene, or xylene. The higher molecular weight paraffinic solvents are better solvents for the polymer than are those of lower molecular weight, and the cyclic hydrocarbons have higher solvent power for the polymers than do the paraffins. After the catalyst has been backwashed sufficiently to remove polymer mechanically and in solution, the flow of the backwashing liquid is terminated, and the vessel is then ready for use in the 1-olefin polymerizing operation. The backwash liquid enters the system through line 22, from a source, not shown, and leaves the system through a line 23 for such disposal as desired. The solvent is preferably heated to a temperature in the range 250 to 500° F., in means not shown, prior to entry into reactor 2 or 3.

When it is desired to recover the 1-olefin polymer, it can be recovered by distilling off the solvent. The solvent can then be reused.

In a modification of my invention, the effluent from the 1-olefin polymerization in reactor 2 or 3 can be vaporized to separate any accompanying polymer as residue, and recondensed prior to passage to alkylation zone 5.

In my process, in general, any known alkylation catalyst, such as sulfuric acid, phosphoric acid, fluid complexes of polyvalent metal halides such as aluminum chloride or aluminum bromide with hydrocarbons, hydrofluoric acid, boron fluoride and mixtures of hydrofluoric acid and boron fluoride can be used. Substantially anhydrous hydrofluoric acid is preferred because of the relative ease with which it can be used and re-used and because of the superior quality of the alkylate that is produced. Known alkylation conditions are employed in the alkylation vessel 5, such as thorough agitation, a temperature in the range of about 30° to 250° F., sufficient pressure to maintain liquid phase conditions, a stoichiometric excess of isoparaffin with respect to the 2-olefin, a reaction time in the range of about 1 to 90 minutes, and the like. When hydrofluoric acid is the catalyst, preferred alkylation conditions comprise agitation of the quality produced by an efficient turbomixer, and overall feed isoparaffin-to-olefin mol ratio in the

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range of about 3:1 to 10:1, a temperature in the range of about 85° to 125° F., and an average residence time in the alkylation zone of about 5 to 30 minutes. After a suitable residence time, the alkylation mixture is passed to the separation zone 9 which may be a centrifuge or a gravity settler. To maintain a proper isoparaffin-to-olefin ratio for optimum alkylate output it is sometimes desirable to add additional isoparaffin over that contained in the original olefin-isoparaffin feed stock. Such isoparaffin can originate from any suitable source, and is passed through line 27 into the alkylator 5.

Such auxiliary apparatus as pumps, valves, regulators, flow controllers, temperature and pressure recording and controlling apparatus have not been shown on the drawing nor described in this specification for reasons of brevity and simplicity. The need for such apparatus, its installation and operation are well understood by those skilled in the art.

Equipment and materials of construction should be selected from those commercially available bearing in mind any corrosive properties of materials and reagents under treatment.

According to a specific embodiment of this invention, a C₄ hydrocarbon fraction is contacted with a chromium oxide catalyst under polymerization conditions and an alkylation feed is subsequently recovered and subjected to alkylation conditions. The C₄ fraction has the following composition:

	Weight percent
Isobutylene -----	10
1-butene -----	20
2-butene -----	20
Isobutane -----	30
Normal butane -----	20

The catalyst is a chromium-oxide-silica catalyst prepared as previously described herein (impregnation of silica-alumina gel composite, drying, and heating in anhydrous air at 930° F. for 5 hours) and has a total chromium content of 4 weight percent and a hexavalent chromium content of approximately 3 weight percent. The silica:alumina ratio in the catalyst is 9:1 on a weight basis.

The above described C₄ fraction is contacted with a fixed bed of the chromium oxide catalyst at a temperature of 190° F., a pressure of 600 p. s. i. and a liquid hourly space velocity of 2. The effluent from the contacting with the chromium oxides catalyst is flashed at 300° F. and atmospheric pressure and the vaporized material is recondensed. The condensate has the following composition:

	Weight percent
Isobutylene -----	2
1-butene -----	5
2-butene -----	22
Isobutane -----	35
Normal butane -----	24
Higher boiling hydrocarbons -----	12

To the condensed material is added sufficient isobutane to provide a mixture having a molar ratio of isobutane to olefins of 5:1. This mixture is pumped into an alkylation reactor provided with a motor-driven turbomixer. Liquid anhydrous hydrogen fluoride is simultaneously supplied to the alkylation reactor. The alkylation reactor is maintained at a temperature of 100° F. and a pressure of 150 p. s. i., the reactants thus being maintained substantially completely in the liquid phase. The residence time of the hydrocarbons in the alkylation reactor is maintained at approximately 15 minutes. The liquid volume ratio of hydrocarbon to hydrogen fluoride in the alkylation reactor is 1:1. The effluent from the alkylation reactor is passed to a settling tank wherein phase separation is effected. The heavier, or hydrofluoric acid, phase is recycled to the reactor. The hydrocarbon phase is washed in sodium hydroxide solution

to remove dissolved hydrogen fluoride. The neutralized hydrocarbon product is fractionated to recover a butane fraction, an alkylate fraction having a boiling range of approximately 100 to approximately 365° F., and a higher boiling or residual fraction. The alkylate fraction is contacted with calcined bauxite at approximately 150° F. and a liquid hourly space velocity of 2, the alkylate being maintained in the liquid phase during the contacting. Thus defluorinated alkylate is recovered as a product of the process and has an ASTM octane number of approximately 90.

After a period of time on stream, the contacting of the butane fraction with the chromium oxide catalyst is discontinued and normal heptane in the liquid phase at a temperature of approximately 300° F. is passed through the chromium oxide catalyst bed to remove accumulated polymer therefrom. The heptane effluent and the accompanying polymer are then subjected to heptane refluxing conditions at atmospheric pressure, a portion of the boiling liquid and accompanying suspended material being continuously withdrawn and subjected to filtration under pressure. The solid removed by filtration is a highly crystalline solid polymer of 1-butene and is useful for the production of molded articles, extruded pipe and tubing and insulation. The filtrate is flashed to remove heptane. The residual material from the flashing is a tacky or semisolid material which is useful as a viscosity index improver for lubricating oils. This material can be improved as a lubricating oil additive by distillation in vacuum to remove materials boiling below 900° F.

While certain process steps, structures, compositions, and examples have been described for purposes of illustration, it is clear that the invention is not limited thereto, and that variation and modification are possible within the scope of the disclosure and the claims.

This application is a continuation-in-part of my application Serial No. 306,343, filed August 26, 1952, now abandoned.

I claim:

1. A process for the selective removal of a 1-olefin from a mixture of hydrocarbons comprising a 1-olefin having from 3 to 8 carbon atoms per molecule and no branching nearer the double bond than the 4-position in admixture with a different olefin, which process comprises contacting said mixture with a chromium oxide catalyst comprising chromium oxide associated with at least one member of the group consisting of silica, alumina, zirconia and thoria, said catalyst having been treated to impart polymerization activity thereto, selectively polymerizing said 1-olefin to high polymer, and recovering a resulting mixture substantially depleted with respect to 1-olefin.

2. A process for the selective removal of a 1-olefin from a mixture of hydrocarbons having from 3 to 5 carbon atoms per molecule and including a 1-olefin, a 2-olefin and an isoparaffin which process comprises contacting said mixture at a temperature in the range 150 to 250° F. with a catalyst comprising from 0.1 to 30 weight percent chromium in the form of chromium oxide, at least part of the chromium being in the hexavalent state, associated with at least one member of the group consisting of silica, alumina, zirconia, and thoria, said catalyst having been activated by heating at an elevated temperature, effecting a selective conversion of 1-olefin to high polymer, and recovering a resulting mixture substantially depleted with respect to 1-olefin.

3. An alkylation process which comprises contacting a mixture comprising a 1-olefin, a 2-olefin, and an isoparaffin and being composed of hydrocarbons having from 3 to 5 carbon atoms per molecule, at a temperature in the range of 150 to 250° F. with a catalyst consisting essentially of from 0.1 to 30 weight percent chromium in the form of chromium oxide of which at least a part of the chromium is in the hexavalent state, associated with at least one member of the group consisting of silica,

alumina, zirconia and thoria, effecting a selective conversion of said 1-olefin to high polymer, recovering said high polymer, recovering a hydrocarbon mixture substantially depleted with respect to said 1-olefin, and subjecting the depleted mixture to alkylation conditions of temperature, pressure and contact time in the presence of a stoichiometric excess of alkylatable isoparaffin with respect to olefins and in the presence of an alkylation catalyst, and recovering a resulting alkylate.

4. A process for the selective removal of a 1-olefin from a mixture of hydrocarbons having from 3 to 5 carbon atoms per molecule and including a 1-olefin, a 2-olefin and an isoparaffin, which process comprises contacting said mixture, at a temperature in the range 170 to 225° F. and a pressure sufficient to maintain the hydrocarbon mixture substantially in the liquid phase, with a catalyst comprising from 0.1 to 10 weight percent chromium as oxide, of which at least part of the chromium is in the hexavalent state, associated with a silica-alumina composite, thus effecting a selective conversion of 1-olefin to tacky polymer, a substantial proportion of which remains in contact with the catalyst, and recovering a resulting mixture substantially depleted with respect to 1-olefin.

5. An alkylation process which comprises contacting a mixture comprising 1-butene, 2-butene and isobutane, at a temperature in the range 170 to 225° F. and a pressure sufficient to maintain the hydrocarbon mixture substantially in the liquid phase, with a catalyst consisting essentially of from 1 to 5 weight percent of chromium as oxide, of which at least part of the chromium is in the hexavalent state, the remainder of said catalyst being a silica-alumina composite, thus effecting a selective conversion of the 1-butene to tacky polymer, recovering said polymer, recovering a hydrocarbon mixture substantially depleted with respect to 1-butene, and subjecting the depleted mixture to alkylation conditions of temperature, pressure, and contact time in the presence of a stoichiometric excess of isobutane with respect to olefins and in the presence of an alkylation catalyst, and recovering a resulting alkylate.

6. An alkylation process which comprises contacting a mixture comprising propylene, 1-butene, 2-butene and isobutane, at a temperature in the range 170 to 225° F. and a pressure sufficient to maintain the hydrocarbon mixture substantially in the liquid phase, with a catalyst consisting essentially of from 1 to 5 weight percent of chromium as oxide, of which at least part of the chromium is in the hexavalent state, said chromium oxide being supported upon a macroporous silica-alumina composite, thus selectively converting propylene and 1-butene to tacky polymer which remains associated with said catalyst, recovering said polymer, passing a resulting hydrocarbon mixture substantially depleted with respect to propylene and 1-butene to an alkylation zone and therein contacting the depleted mixture with a hydrofluoric acid alkylation catalyst in the presence of a substantial stoichiometric excess of isobutane with respect to olefins at temperature and pressure conditions suitable for the alkylation of said isobutane, and recovering a resulting alkylate.

7. A process according to claim 6 wherein said polymer is recovered by contacting the chromium oxide catalyst with a solvent for said polymer and recovering said polymer from admixture with said solvent.

8. A process for the polymerization and alkylation of a mixture of hydrocarbons having from 3 to 5 carbon atoms per molecule and including a 1-olefin, a 2-olefin, and an isoparaffin, which process comprises contacting said mixture, at a temperature in the range 170 to 225° F. and a pressure sufficient to maintain the hydrocarbon mixture substantially in the liquid phase, with a catalyst comprising from 0.1 to 10 weight percent chromium as oxide, of which at least part of the chromium is in the hexavalent state, associated with a silica-alumina com-

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posite, thus effecting a selective conversion of 1-olefin to tacky polymer, recovering said polymer, recovering a hydrocarbon mixture substantially depleted with respect to 1-olefin, and subjecting the depleted mixture to alkylation conditions of temperature, pressure, and contact time in the presence of a stoichiometric excess of isoparaffin with respect to olefins and in the presence of an alkylation catalyst, and recovering a resulting alkylate.

9. An alkylation process which comprises contacting a mixture of hydrocarbons having from 3 to 5 carbon atoms per molecule and including a 1-olefin, a 2-olefin and an isoparaffin, at a temperature in the range 170 to 225° F. and a pressure sufficient to maintain the hydrocarbon mixture substantially in the liquid phase, with a catalyst comprising, as an essential ingredient, from 0.1 to 10 weight percent of chromium as oxide, of which at least part of the chromium is in the hexavalent state, the remainder of the catalyst being at least one oxide selected from the group consisting of silica, alumina, zirconia, and thoria, thus effecting a selective conversion of 1-olefin to tacky polymer, recovering a hydrocarbon mixture substantially depleted with respect to 1-olefin, subjecting the depleted mixture to alkylation conditions of temperature and pressure in the presence of a stoichio-

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metric excess of isoparaffin with respect to olefins, and recovering a resulting alkylate.

10. A process for the selective removal of a 1-olefin from a mixture of hydrocarbons comprising a 1-olefin having from 3 to 8 carbon atoms per molecule and no branching nearer the double bond than the 4-position in admixture with a different olefin, which process comprises contacting said mixture, under polymerization conditions of temperature, pressure, and contact time, with a chromium oxide catalyst comprising chromium oxide, in which at least part of the chromium is hexavalent, associated with at least one member of the group consisting of silica, alumina, zirconia, and thoria, selectively polymerizing said 1-olefin to high polymer, and recovering a resulting mixture substantially depleted with respect to 1-olefin.

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