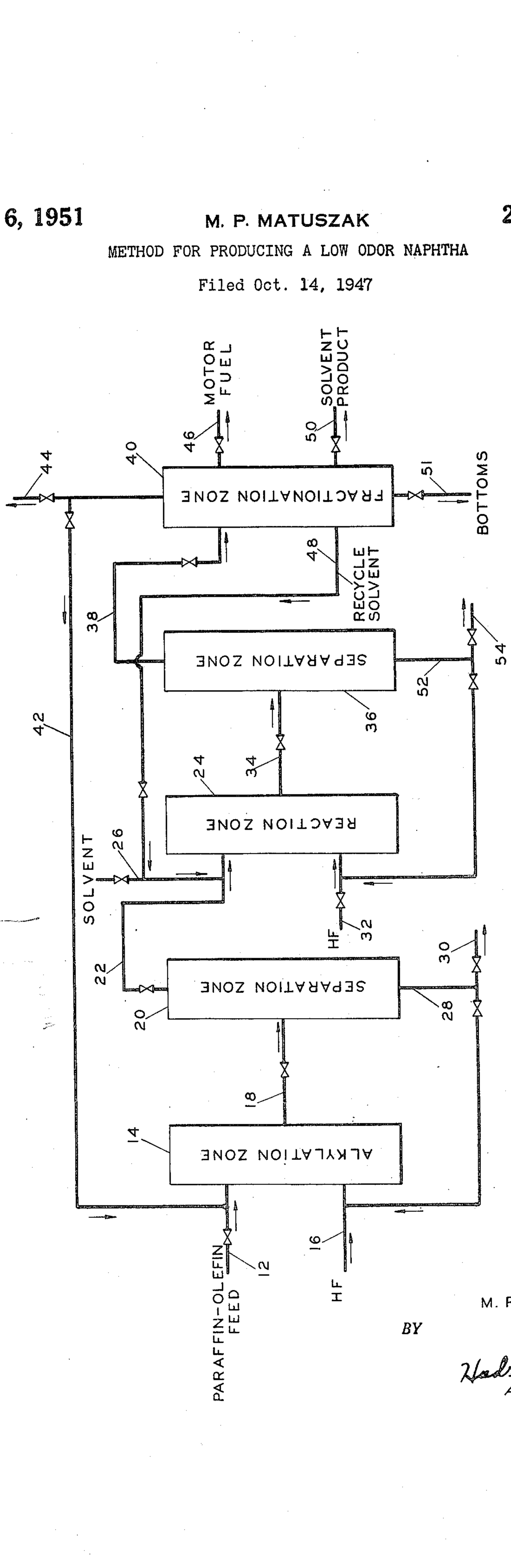
March 6, 1951 M. P. MATUSZAK 2,544,559

METHOD FOR PRODUCING A LOW ODOR NAPHTHA

Filed Oct. 14, 1947



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Patented Mar. 6, 1951 2,544,559

UNITED STATES PATENT OFFICE

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METHOD FOR PRODUCING A LOW ODOR NAPHTHA

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Application October 14, 1947, Serial No. 779,738

8 Claims. (Cl. 260—683.4)

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This invention relates to the production of high-boiling saturated naphtha. In one embodiment it relates to the production of solvent naphthas having a low odor. In one specific embodiment it relates to contacting malodorous solvent-type hydrocarbon material with the hydrocarbon effluent from a hydrofluoric acid alkylation process in the presence of hydrofluoric acid as a catalyst.

Many hydrocarbon materials are unsuitable or at least somewhat objectionable for use as solvents or vehicles for paints, sprays, insecticides, printing inks, or the like, or for use as cleaning solvents, or the like, because of an objectionable odor. This odor in many instances appears to be produced mainly by olefinic material, aromatics, sulfur compounds, nitrogen-containing bodies and the like. In the past, many attempts to deodorize such hydrocarbon materials, as by treatment with sulfuric acid or fuller's earth, have been only partially successful, mostly because of an excessive consumption of the hydrocarbon material.

I have discovered a simple and economical method of manufacturing low-odor hydrocarbon solvents by contacting high-boiling, straight-run naphtha, kerosene, or the like, with the hydrocarbon effluent from a paraffin-olefin catalytic alkylation process in the presence of an alkylation catalyst, such as hydrofluoric acid. By this method the odor producing bodies, particularly the easily alkylatable high-odor bodies, such as aromatic-type hydrocarbons contained in such naphthas, are removed. I have also discovered that the odor-producing bodies in such naphthas concentrate in the lower-boiling fraction of the treated naphtha, as a result of which the low-boiling portion of the treated naphtha may be recycled to the contacting step for further treatment. By this means the odor producing bodies are substantially removed from the naphtha treated.

An object of this invention is to provide a method for producing high-boiling saturated naphtha.

Another object of this invention is to provide a process for the production of substantially odorless, high-boiling naphthas, suitable for use as insecticide bases and the like.

Another object of this invention is to provide a simple and economical process for manufacturing substantially odorless naphtha.

Other objects and advantages will be apparent to one skilled in the art from the accompanying disclosure and discussion.

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I have discovered that kerosene or other heavy straight-run naphtha can be converted into a valuable odorless naphtha which is very much in demand by contacting such a naphtha with the hydrocarbon effluent material from a paraffin-olefin catalytic alkylation process in the presence of an alkylation catalyst, such as hydrofluoric acid or sulfuric acid. In the present invention a heavy straight-run naphtha obtained by non-cracking distillation of a selected crude oil is treated in the presence of the hydrocarbon effluent from a paraffin-olefin catalytic alkylation process wherein the odor of said straight-run naphtha is removed, as well as the improvement of other qualities of the naphtha which make it more desirable for use as a cleaner's naphtha, insecticide base and the like. In one embodiment of my invention a straight-run naphtha boiling above about 300° F. is added to the hydrocarbon effluent from a hydrofluoric acid alkylation process in which a paraffin such as isobutane is reacted with an olefin, such as butene. By using a naphtha boiling above 300° F., it is readily separable from the motor fuel alkylation product boiling up to about this temperature by fractional distillation. When so separated the product usually contains a small proportion of heavy alkylate, boiling above 300° F., which is itself suitable for use as an odorless solvent of the preferred type.

The exact chemical reactions which take place in my process are not definitely known; however, it is believed that the aromatics, unsaturated compounds and non-hydrocarbon organic compounds present in the original naphtha are removed by alkylation and/or polymerization reactions; possibly sulfur- and nitrogen-containing compounds are removed by formation of heavy complexes with the catalyst employed and removed from the process as catalyst-soluble oils. In any event, such deleterious compounds are removed from the original naphtha and a substantially odorless product is obtained.

My invention is particularly advantageous because odorless naphthas, which are very much in demand, can be prepared from kerosene or straight-run naphthas by introducing such material into the hydrocarbon effluent from a hydrofluoric acid alkylation process, which process is operating in a manner to produce motor or aviation fuel components. The naphtha charged to such a process usually has a boiling range higher than the motor or aviation fuel components produced in the alkylation process and is recovered as odorless naphtha in high yields maintaining

substantially the same boiling range as the original naphtha charged. Therefore it can easily be separated from the alkylation products by distillation. The only significant change in the naphtha charged is that the odor-producing bodies are removed or changed so that the odor is nullified.

The process of my invention may be carried out under usual catalytic alkylation conditions which, for the preferred mineral acid catalysts, include a temperature in the range of about 50 to about 140° F.; however, a temperature between about 75 and about 110° F. is preferable. A pressure sufficient to maintain liquid phase in the reaction zone is satisfactory but usually I prefer a pressure in the range of about 50 to about 125 pounds per square inch. The straight-run naphtha employed in my process may vary considerably as to boiling range. For example, the naphtha employed may have a boiling range from about 300 to about 550° F.; however, one coming in the boiling range of about 325 to about 450° F. is usually preferable. The contact time of the hydrocarbons with the catalyst in the reaction zone may vary considerably depending upon the specific hydrocarbon material, the catalyst and the operating conditions employed, but usually a contact time in the range of about 5 to about 60 minutes is satisfactory; however, a higher or lower contact time may be desirable in certain cases. The volume ratio of hydrocarbon to catalyst used is in the range of about 1:0.25 to about 1:1.5; however, a ratio of 1:1 is preferable. Although the process of my invention for producing odorless naphthas may be conducted in the presence of any paraffin-olefin alkylation catalyst, for example, concentrated sulfuric acid or one or more aluminum chloride-hydrocarbon complexes, I prefer to use anhydrous hydrofluoric acid as the catalyst.

One convenient and economical procedure by which odorless naphthas suitable for use in insecticide bases and the like can be made in accordance with my invention is to introduce a straight-run naphtha into the hydrocarbon effluent from a hydrofluoric acid alkylation process, which process is producing motor or aviation fuel components. Such a process usually employs isobutane and butenes as reactants; however, other isoparaffins and olefins may be used, for example, isopentane and propylene. The amount of naphtha added to the hydrocarbon effluent from such a process may vary from about 1 to about 20 per cent by weight of the total hydrocarbon effluent, depending on such factors as the quantity of the odorless naphtha desired, particular catalyst used and the like, but usually about 5 to about 10 per cent by weight is preferable.

The accompanying diagrammatic drawing illustrates one specific embodiment of the process of my invention. Referring to the drawing the paraffin-olefin feed to the alkylation process, which feed, for the purpose of illustration, comprises butane and butenes and is passed through line 12 to alkylation zone 14 where it is contacted with anhydrous hydrofluoric acid entering the alkylation zone through line 16. The contents of alkylation zone 14 are mixed by any suitable means and are maintained under alkylation conditions so as to obtain the desired alkylation reaction. The resulting reaction mixture passes through line 18 to separation zone 20 where it is separated into an acid phase and a hydrocarbon phase. The acid phase is recycled through line 28 to alkylation zone 14 or at least a portion of the acid phase may be withdrawn from the system through line 30 for use elsewhere, as desired. The hydrocarbon phase from separation zone 20 passes through line 22 to reaction zone 24. A solvent-type malodorous straight-run naphtha is introduced through line 26 into reaction zone 24 by way of line 22. Anhydrous hydrofluoric acid is introduced into reaction chamber 24 by way of line 32. The contents of reaction zone 24 are mixed by any suitable means to obtain the desired reactions to improve the odor of the solvent introduced therein. The resulting reaction mixture passes through line 34 to separation zone 36 where it separates into an acid phase and a hydrocarbon phase. The acid phase may be recycled through line 52 to reaction zone 24 or at least a portion of said acid phase may be removed from the system through line 54 for use elsewhere as desired. The hydrocarbon phase from reaction zone 36 is passed through line 38 to fractionation zone 40. A light fraction consisting chiefly of the paraffin contained in the original feed stock is recycled to alkylation zone 14 by way of line 42. A portion of this light material may be removed from the system through line 44, if desired. A motor fuel fraction is removed from fractionation zone 40 through line 46. The light treated solvent product is removed from fractionation zone 40 and is recycled to reaction zone 24 by way of lines 48 and 26. The desired solvent product is removed from fractionation zone by way of line 50 and the heavy bottoms are removed through line 51.

In some cases the treated naphtha retains a small but objectionable amount of odor. A modification that is advantageous in such cases is to fractionate the product to obtain a low-boiling fraction, boiling between say 300 and 350° F. (or thereabouts, as may be determined by experiment), which contains substantially all the surviving odoriferous compounds, and to withdraw this fraction from the system or recycle it to the catalyst treating zone. Ordinarily less than one-fourth of once-treated product retains enough odor to warrant recycling in this manner, and this fraction generally appears to be the lowest-boiling part of the once-treated product; therefore, it is readily separable by fractional distillation. The material boiling above this low-boiling fraction may be withdrawn as an odorless product, but at times it may be preferably distilled to obtain fractions of desired narrow boiling ranges or to free it from a small proportion of undesirably high-boiling compounds, which are withdrawn as a heavy product.

In some cases a small portion, not exceeding about 1 per cent by weight of the original naphtha, of a relatively easily alkylatable aromatic material, such as benzene or furan, may be introduced into the original naphtha prior to its entry into the treating zone. This may be done when the original naphtha, such as straight-run is relatively free of easily alkylatable aromatics. These easily alkylatable compounds may react with certain of the odor-producing bodies, as well as the alkyl fluorides in the hydrocarbon effluent materials from the alkylation process, thereby improving the odor and other qualities of the finished solvent. Also, these easily alkylatable compounds may be introduced into the recycle treated solvent, as that fraction contains the major portion of the odor-producing bodies remaining in the treated solvent. The resulting reaction products may be removed from the finished solvent by distillation, either as a motor fuel frac-

tion or as heavy bottom product, depending upon the boiling range. Before the easily alkylatable compounds are added to the original naphtha or the recycle treated solvent, it should be determined by experiment, beforehand, if the resulting reaction products can be removed by distillation. It is necessary that they be removed from the finished solvent product, as such compounds have a characteristic odor which make them undesirable in the finished solvent. The boiling range of such reaction product may be determined by experiment in each case in order to determine whether or not these reaction products will fall in the boiling range of the desired solvent.

In the above mentioned drawing reference to certain equipment such as pumps, gauges and the like, which obviously would be necessary to actually operate the process have been intentionally omitted. Only sufficient equipment has been shown to illustrate the process and it is intended that no undue limitation be read into this invention by reference to the drawing and discussion thereof.

EXAMPLE

To a hydrocarbon effluent material produced in a hydrofluoric acid alkylation process in which isobutane and butenes are used as alkylatable materials is added a solvent-type odoriferous straight-run naphtha having a boiling range of 300 to 425° F. in the amount of 10 per cent by volume based on the hydrocarbon effluent material. The mixture is passed to a reactor where it is intimately mixed by means of a mechanical stirrer with an equal volume of anhydrous hydrofluoric acid at a temperature of about 100° F. and at a pressure of about 75 pounds per square inch for a period of time of about 15 minutes. The resulting reaction mixture is passed to a settler from which the hydrofluoric acid phase is recycled to the reactor and from which the hydrocarbon phase is passed to a series of fractionation steps for separation into recycle by-product and product fractions. The solvent-type product boiling above 300° F. is substantially odorless. Data for this product are summarized in the table; for comparison, data for the original straight-run naphtha used are include.

Table

	300–425° F. Straight-Run Naphtha	Low Odor Solvent Product
Yield, weight per cent of 300–425° F. Straight-Run Naphtha.	----------	99.
ASTM distillation, °F.:		
First drop	300	325.
10% evap	313	334.
50% evap	343	361.
90% evap	389	447.
End point	425	546.
Gravity, API	49.8	48.4.
Specific gravity (20/4)	0.7778	0.7833.
Refractive index (20/D)	1.4351	1.4379.
Sulfur, weight per cent	0.141	0.0448.
Nitrogen, weight per cent	0.44	0.11.
Bromine number	1.1	0.28.
ASTM octane number	26.9	32.
Color	Amber	Almost colorless.
Odor	Strong	Slight.

The product is markedly improved with respect to odor. The slight surving odor appears to be due to some surviving sulfur and/or nitrogen compounds; however, these compounds are greatly reduced by the treatment. The distillation data indicate that the yield would exceed 100 per cent if the initial boiling (first drop) point is made as low as for the original 300–425° F. straight-run naphtha fraction.

It is to be understood that this invention should not be unnecessarily limited to the above discussion and description and that modifications and variations may be made without departing substantially from the invention or from the scope of the claims.

I claim:

1. A method for producing a low-odor naphtha which comprises admixing a straight run naphtha having a boiling range within the limits of 300 to 550° F. and containing odor-producing compounds, with hydrocarbon effluent recovered from a zone of an isoparaffin-olefin alkylation conducted in the presence of a liquid alkylation catalyst, contacting the resulting hydrocarbon admixture with a liquid alkylation catalyst at a temperature within the range of from 50 to 150° F., a pressure in the range of from 50 to 125 p. s. i. g. for a contact time within the limits of from 5 to 60 minutes, separating a hydrocarbon phase from effluent of the last said contacting, from said hydrocarbon phase separating an alkylate fraction boiling in the motor fuel range, a naphtha fraction boiling above said motor fuel range and not higher than 550° F., and a residual fraction boiling above 550° F., said naphtha fraction comprising said straight run naphtha freed of a major portion of its odor producing components together with a minor portion of alkylate formed in said alkylation zone, said naphtha fraction containing surviving odor producing compounds concentrated in a lowest boiling portion thereof and having a volume not exceeding 25 per cent of the volume of said straight run naphtha, separating said lowest boiling portion from said naphtha fraction, and recovering a low-odor naphtha fraction boiling in a range above that of said lowest boiling portion and below 550° F. as a product of the process.

2. A process as in claim 1 wherein the catalyst used is sulfuric acid.

3. A process as in claim 1 wherein the catalyst is hydrofluoric acid.

4. A process as in claim 1 wherein the catalyst is an aluminum chloride-hydrocarbon complex.

5. The process of claim 1 wherein said lowest boiling portion has a boiling range within the limits of 300 and 350° F.

6. A method for producing a low-odor naphtha which comprises contacting isobutane with a butene in an alkylation zone under alkylation conditions employing anhydrous hydrofluoric acid as an alkylation catalyst, separating effluent from said alkylation zone into a hydrofluoric acid-rich phase and a hydrocarbon-rich phase, admixing hydrocarbon thus separated with from 1 to 20 per cent of its weight of a malodorous straight run naphtha having a boiling range within the limits of 300 to 550° F., contacting a resulting hydrocarbon admixture with anhydrous hydrofluoric acid in a liquid volume ratio of total hydrocarbon to hydrofluoric acid within the limits of 1:0.25 to 1:1.5 at a temperature within the limits of from 50 to 150° F., a pressure within the limits of 50 to 125 p. s. i. g. and for a contact time within the limits of from 5 to 60 minutes, separating effluent from the last said contacting into a hydrocarbon-rich phase and a hydrofluoric acid rich phase, fractionating the last said hydrocarbon phase and recovering as products of said fractionating an alkylate fraction boiling in the motor fuel range, a naphtha

fraction boiling above said motor fuel range and not higher than 550° F., and a residual fraction boiling above 550° F., said naphtha fraction comprising said malodorous naphtha freed of a major proportion of its odor producing bodies together with a minor proportion of alkylate formed in said alkylation zone, said naphtha fraction containing surviving odor producing bodies concentrated in a lowest-boiling portion thereof having a volume not exceeding 25 per cent of the volume of said malodorous naphtha initially admixed as above described, separating said lowest boiling portion from said naphtha fraction and recycling a lowest boiling portion thus separated to the zone of the last said contacting, and recovering a low-odor naphtha fraction boiling in a range above that of said lowest boiling portion and below 550° F. as a product of the process.

7. A method for producing a low-odor naphtha from a malodorous straight run naphtha having a boiling range within the limits of 300–550° F. and devoid of easily alkylatable materials, comprising adding not more than one per cent of an easily alkylatable aromatic hydrocarbon to such a malodorous naphtha, based on the weight of said naphtha, admixing the resulting aromatic-naphtha with hydrocarbon effluent recovered from a zone of an isoparaffin-olefin alkylation conducted in the presence of a liquid alkylation catalyst, contacting the resulting total hydrocarbon admixture with a liquid alkylation catalyst at a temperature within the range of from 50 to 150° F., a pressure in the range of from 50 to 125 p. s. i. g. for a contact time within the limits of from 5 to 60 minutes, separating a hydrocarbon phase from the effluent of the last said contacting, from said hydrocarbon phase separating a hydrocarbon fraction boiling in the motor fuel range, a naphtha fraction boiling above said motor fuel range and not higher than 550° F., and a residual fraction boiling above 550° F., said naphtha fraction comprising said malodorous naphtha freed of a major proportion of its odor producing components together with a minor proportion of alkylate formed in said alkylation zone and said residual fraction, said naphtha fraction containing surviving odor producing compounds concentrated in a lowest boiling portion thereof having a volume not exceeding 25 per cent of the volume of said straight run naphtha, separating said lowest boiling portion from said naphtha fraction, separating said residual fraction from said naphtha fraction, and recovering a low-odor naphtha fraction boiling in a range above that of said lowest boiling portion and below 550° F. as a product of the process.

8. A method for producing a saturated low-odor naphtha from an alkylatable paraffin, an olefin, and a straight run naphtha containing malodorous alkylatable hydrocarbons, comprising contacting said paraffin with said olefin under alkylating conditions utilizing a liquid alkylation

catalyst, said paraffin reacting with said olefin to form alkylate boiling in and above the motor fuel boiling range and containing alkylating materials as by-product impurities, recovering hydrocarbon effluent from the zone of said paraffin-olefin reacting, contacting effluent thus recovered with from 1 to 20 per cent of its weight of such a naphtha as above described having a boiling range within the limits of 300 to 425° F. in the presence of a liquid alkylation catalyst in a volume ratio of total hydrocarbon to catalyst within the limits of 1:0.25 to 1:1.5, at a temperature within the limits of 75 to 110° F., a pressure within the limits of 50 to 150 p. s. i. g. for a period of from 5 to 60 minutes, whereby malodorous alkylatable hydrocarbons in said naphtha react with by-product alkylating materials in said effluent to form heavy alkylate having a boiling range above 550° F., recovering hydrocarbon effluent from the zone of the last said contacting, separating hydrocarbon boiling in the motor fuel range and below 300° F. from the last said effluent, the resulting residual fraction of the last said effluent comprising said straight-run naphtha freed of a major proportion of its odor producing bodies together with a minor proportion of alkylate formed during said paraffin-olefin contacting, and said heavier alkylate, said resulting residual fraction containing unreacted odor-producing bodies originally present in said straight run naphtha concentrated in a lowest boiling portion having a boiling range not exceeding 325° F., recovering said lowest boiling portion and recycling same to the zone of the last said contacting, separating said heavy alkylate from said residual fraction, and recovering as a product of the process a low odor naphtha boiling in a range above that of said lowest boiling portion and not higher than 550° F. and comprising said straight-run naphtha free of its odor producing bodies together with a minor proportion of alkylate formed during said paraffin-olefin contacting, the volume of the recovered low-odor naphtha being equal to at least 99 per cent of the volume of said straight-run naphtha initially admixed with alkylation effluent as above described.

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