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TREATMENT OF HYDROCARBON OILS

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1 Claim. (Cl. 196—24)

This invention relates particularly to the treatment of hydrocarbon distillates of gasoline boiling range and more specifically to a method of treatment whereby the sulfur content of such distillates may be reduced without undesirably affecting other necessary properties. In some instances the treatment may improve the quality of the oils treated in other ways than reducing the sulfur content. For example, there may be reductions in actual and potential gum content, color, and antiknock value.

Desulfurization is one of the major problems confronting the petroleum industry since many crude petroleums, particularly those of a naphthenic or mixed base character, contain such quantities of sulfur that motor fuel made from them by straight distillation without cracking, and particularly those made by cracking their heavier distillates and residua, frequently contain so much sulfur that their use, without special treatment, is impossible since not only do the sulfur compounds impart a foul odor which is undesirable from a sales standpoint, but the sulfurous and sulfuric acids formed by oxidation of the gasolines in the cylinders of internal combustion engines frequently cause serious crank case corrosion, and the sulfur in the unburned gasolines corrodes feed lines, carburetor parts, etc. Although the limits of sulfur tolerance have been raised, due to better ventilation of crank cases, within the last few years, there are still definite limits to the total sulfur which is allowable in gasolines for use in internal combustion engines.

When the sulfur problem was first encountered in motor fuels, along with other problems peculiar to the treatment of cracked gasolines, such as improvement in color and gum content, the principal treatment in vogue was with sulfuric acid which was generally highly effective in improving the color and odor of straight run paraffinic and mixed base gasolines. But it was found that the use of sulfuric acid was seldom selective in improving any one property such as color. For example, if color was improved to a desired point, there was frequently large losses due to solution and ester formation of olefinic compounds present. Similarly, attempts to desulfurize with sulfuric acid to meet the usual requirements of 0.10% sulfur caused extremely high losses and the formation of such compounds as sulfonic acids, sulfones, sulfur ethers etc. which remained dissolved in the gasoline, and were only partially removed by treatment with alkalis, clay filtration, or rerunning of the acid-treated stocks. Desulfurization by the use of sulfuric acid therefore was found to have, and still has very limited application.

Among the methods which have been tried to effect selective desulfurization of cracked gasolines without adversely affecting other properties of such gasolines, particularly anti-knock value due to removal or conversion of unsaturated compounds of relatively high antiknock value, is hydrogenation in the presence of catalysts under moderate temperature and pressure conditions. Heretofore, attempts to desulfurize cracked distillates by this method have generally met with failure because of the fact that the addition of hydrogen to unsaturated hydrocarbons apparently proceeded concurrently and excessively with the action of hydrogen on sulphur compounds of various types so that by the time the sulfur was reduced to the allowable maximum by the formation principally of hydrogen sulfide (evolved as a gas), the antiknock value of the gasoline has been seriously and permanently impaired by the saturation of olefinic hydrocarbons. This has been particularly notable in prior attempts to desulfurize gasoline boiling range liquids made by the polymerization of the olefins in hydrocarbon gas mixtures containing sulfur compounds, since the olefins are readily hydrogenated, and as a rule their paraffinic counterparts have lower antiknock value. Another difficulty in prior attempts to desulfurize without serious loss of antiknock value has been the gradual, and sometimes rapid, deterioration of hydrogenation catalysts employed due to the formation of sulfides having reduced or no hydrogenating activity. It is with improvements in desulfurizing sulfur-containing gasolines by means of hydrogenation that the present invention is concerned.

In one specific embodiment, the present invention comprises a process for desulfurizing gasolines containing both olefinic hydrocarbons and sulfur compounds which comprises subjecting the vapors of said gasolines mixed with relatively large amounts of hydrogen to contact with nickel sulfide catalysts at temperatures within the approximate range of 250–450° C. and superatmospheric pressure of the order of 300 pounds per square inch or higher while using relatively low liquid space velocities.

We have found that when using nickel sulfide catalysts while observing the conditions of operation specified that cracked gasolines containing both sulfur compounds and olefins can be desulfurized to an extent so that they are read-

ily marketable without adversely affecting antiknock value. As will be shown in later examples, a relatively large excess of hydrogen over that necessary for effecting complete hydrogenation of the olefins and removal of sulfur is necessary and if antiknock losses are to be minimized, the degree of olefin hydrogenation must be stopped at a definite point depending upon the composition of the gasolines treated in respect to sulphur and olefinic content.

While the scope of the present invention is not to be in any way limited by the theory expressed, it is considered to be possible that in the presence of a large excess of hydrogen and under the other limiting conditions of operation, the rate of desulfurization reaction increases out of proportion to the rate of olefin hydrogenation reaction so that effective sulfur removal is accomplished before undesirable olefin hydrogenation has occurred. Other possible factors are the rate of hydrogenation of various types of olefins, both normal and isomeric, but these are somewhat unpredictable, particularly in the complicated mixtures in which they occur in cracked gasoline. In some instances highly branched olefin hydrocarbons show greater antiknock after hydrogenation to the corresponding paraffins although this rule is by no means absolute. Relatively low liquid space velocities are preferable of the order of 0.5 to 5 depending upon the chemical and physical characteristics of the gasoline treated. It is to be noted that the temperatures and pressures employed are of moderate order.

It has been found when using nickel sulfide catalysts in desulfurizing sulfur-containing oils by limited hydrogenation reactions that substantially no difficulties are encountered with catalyst poisoning, and operations may be conducted over long periods of time before reactivation is necessary due to the deposition of carbonaceous materials. After such a point is reached, reactivation is readily practiced by passing air or other oxidizing gas mixtures over the spent catalyst to burn off the carbonaceous deposits. During this step some of the nickel sulfide will be found to lose sulfur dioxide and sulfur trioxide to form nickel oxide which is later reduced to metal by hydrogen in a subsequent operating period, and eventually sulfurized to nickel sulfide by the sulfur in the gasoline. Whatever nickel sulfide is oxidized to sulfate will be reduced to sulfide by the hydrogen present during the operating stages.

While it is preferred to start with nickel sulfide catalysts in operating the process, it is comprised within the scope of the invention to start with nickel which is gradually sulfurized during the process or deliberately sulfurized prior to the inception of the process by passing hydrogen sulfide or some other decomposable sulfur compound, either inorganic or organic, through the granular material. The catalytic sulfide may be employed on carriers or spacing agents of a relatively inert and usually siliceous refractory character. Besides frequently used siliceous carrying materials such as diatomaceous earth, clays, bentonites, montmorillonites, both raw and acid treated, crushed refractories, etc., other carriers such as properly prepared alumina, chromium oxide, titanium oxide, cerium oxide, thorium oxide, and zirconium oxide, and even high melting salts such as calcium phosphate, aluminum phosphate, etc. may be used.

A convenient method of preparing suitable catalysts consists in precipitating nickel hydroxide or carbonate on a support suspended in a solution of a nickel salt to which a precipitant is added, the deposited compound being later reduced to nickel which is then sulfurized, or the hydroxide or carbonate, etc. may be directly sulfurized without intermediate reduction. It is also comprised within the scope of the invention to form catalysts by precipitating nickel sulfide directly upon suitable granular supports or by incorporating nickel sulfide with finely divided supporting materials followed by pelleting or otherwise forming of the particles of usable size. As a further alternative, preformed supports such as pellets may be impregnated with nickel salts and these composites sulfurized by any necessary method to produce a usable catalyst.

A convenient method of preparing a nickel sulfide catalyst for use according to the present process consists in producing an extremely active reduced nickel catalyst supported on inert carrying material in pelleted form, the metal being sulfurized by the use of hydrogen sulfide or sulfur-containing hydrocarbon vapors.

The general method of preparation of such a catalyst involves the following steps: Kieselguhr is suspended in a relatively dilute aqueous solution of nickel sulfate and a saturated hot solution of sodium carbonate is added gradually with constant agitation, the proportions of kieselguhr, nickel sulfate, and sodium carbonate being chosen so that after washing and drying the precipitate, pelleting with graphite and reducing with hydrogen, an approximate composition corresponding to that given below is obtained.

	Per cent
Total nickel	62.0
Oxygen in nickel oxide (NiO)	4.0
Graphite	6.0
Kieselguhr	28.0

It is only necessary to employ commercially pure sodium carbonate and nickel sulfate in the primary precipitation, although for best results the reactions are brought about in distilled water which can be obtained by the condensation of ordinary plant system. As a rule a considerable excess of sodium carbonate is employed corresponding to approximately 1.7 moles to 1 mole of anhydrous nickel sulfate. It is important that the temperature of the suspension of kieselguhr and nickel sulfate solution be kept low and therefore the hot saturated sodium carbonate solution is added gradually so as to prevent a noticeable rise in temperature.

The primary precipitate consists of kieselguhr, nickel carbonate and nickelous hydroxide, the composition of the particles of the precipitate without the silica corresponding to the approximate formula $2NiCO_3.7Ni(OH)_2.7H_2O$. It is probable that some of the water in this formula is associated with the kieselguhr. The relative amounts of carbonate, hydroxide, and water will depend to some extent upon the conditions of drying.

The dry precipitate may now be mixed with 4% of its weight of powdered graphite or other suitable lubricant and pelleted into small cylindrical forms of approximately $\frac{7}{32}$'' diameter and $\frac{1}{8}$'' thickness in any standard type of pelleting machine. The graphite or other lubricant is added to lubricate the pelleting machine and eliminate sticking of the pellets, and in the percentage shown has no deleterious effect upon the catalytic activity of the pellets. The approxi-

mate composition of the material at this point is given below:

	Per cent
Total nickel	40
Carbon dioxide	7
Total water	20
Oxygen in nickel oxide (NiO)	11
Graphite	4
Kieselguhr	18

The formed pellets which still contain the mixture of carbonate and hydroxide are now heated in a stream of air or nitrogen at a temperature of approximately 300° C. (572° F.) to eliminate carbon dioxide. At this temperature it has been found that there is substantially no oxidation of the graphite. After the requisite amount of carbonate decomposition has ben effected, the reduction of the nickel oxides is conducted at increasing temperatures in a stream of hydrogen until a temperature of approximately 425° C. (800° F.) is reached, the reduction being continued until approximately 76% of the oxides have been reduced to nickel which gives a material having the composition shown in the second preceding tabulation. Analyses have indicated that in the formation of the catalyst composite of the preferred composition the following reactions take place in the decarbonizing and reduction steps:

(I) $2NiCO_3.7Ni(OH)_2.7H_2O \rightarrow 9NiO+2CO_2+14H_2O$

(II) $9NiO+7H_2 \rightarrow 7Ni+2NiO+7H_2O$

In the heating and reduction steps the porosity and hence the contact surface of the composite catalyst pellets is greatly increased and the crushing strength of the pellets is reduced to approximately 50% of their original value, this still being sufficiently high enough so that the pellets may be used in beds of reasonable depth in practice without crushing to produce fines. The pelleted material is then sulfurized by passing hydrogen sulfide thereover at a moderate temperature.

In the general operation of the process, sulfur-containing gasoline is vaporized, mixed with a relatively large excess of hydrogen or gases having a high hydrogen content, and the mixture is preheated to a temperature within the range previously specified and passed over granular nickel sulfide catalyst at a rate determined by trial to produce the best results. It is to be recognized that each charging stock will require a different combination of operating variables to produce optimum results in respect to decomposition of organic sulfur compounds and hydrogenation of unsaturated hydrocarbons. The invention is not limited to any particular type of apparatus but may utilize any of those found to be suitable, either those of conventional type or of special design.

To illustrate the type of results normally obtainable in the operation of the present process, the following examples are introduced but without the intention of unduly limiting the scope of the invention in exact correspondence with the data presented.

Example I

A gasoline was treated which had been produced by catalytically cracking a gas oil distillate from an East Texas crude oil. Vapors of the gasoline at a temperature of 350° C. (662° F.) were injected into hydrogen at the same temperature under a pressure of 900 pounds per square inch and passed over a supported nickel sulfide catalyst at a liquid space velocity of 1.

The following tabulation shows the results obtained in a run made to determine the degree of olefin hydrogenation which could be tolerated before appreciable loss in antiknock value occurred.

Period	Hours on stream	Bromine number	Hydrogenation, percent	Sulfur in product, percent	Octane number
Chg. Stk.		121		0.06	80.5
1	8	1	99.3	0.004	
2	16	3	97.7	0.007	
3	32	4	96.8	0.008	
4	40	3	97.7	0.008	
5	48	6	95.2	0.007	67.5
6	96		60.0	0.015	80.5

The catalyst employed in the run which furnished the above data was incompletely sulfurized at the outset of the run and therefore apparently had too high an activity so that excessive hydrogenation of the olefins occurred with a corresponding drop in octane number as shown after the fifth period of operation. As the catalyst became more highly sulfurized the octane number in the product was regained while the sulfur was still being reduced notably. The following data shows the comparison of properties of the charging stock and the product being produced at the end of the run:

	Chg. stock	Product
Ind. period, oxygen bomb test, minutes	55	1,4440+
Copper dish gum, mg./100 cc.	69	11
A. S. T. M. gum, g/100 cc.	7	3
Color, Saybolt	Yellow	27
Color stability	Yellow	19
Doctor test	Positive	Negative

Desulfurization of California cracked gasoline—Exploratory runs

Operating conditions:				
Temperature, °C.	350	350	350	350
Temperature, °C.	662	662	662	662
Hydrogen press., lbs./sq. in.	300	300	900	900
Liquid space velocity per hour	1.6	1.3	1.3	1.2
Bromine number:				
Original charge	63	63	63	63
Product	40	37	25	11
Sulfur, weight percent:				
Original charge	1.17	1.17	1.17	1.17
Product	0.25	0.12	0.16	0.06
Hydrogen, cu. ft./bbl.:				
Hydrogen consumed by sulfur	29	33	32	35
Hydrogen consumed by olefin	171	189	278	385
Hydrogen consumed, total	200	222	310	420
Exit hydrogen from plant	200	1,535	325	1,860

The following tabulation of data summarizes runs using optimum conditions:

Desulfurization of California cracked gasoline, using optimum conditions as predicted from exploratory runs

Operating conditions:		
Temperature, °C.	350	350
Temperature, °F.	662	662
Hydrogen pressure, lbs./sq. in.	300	300
Liquid space velocity per hour	1.3	2.7
Original charge:		
Bromine number	63	63
Sulfur, weight, percent	1.17	1.17
Octane number	72	72
Octane number+1 cc. T. E. L.[1]	75	75
Octane number+3 cc. T. E. L.	77	77
Product:		
Liquid yield, volume, percent	96	98
Bromine number	[2] 21	[3] 47
Sulfur, weight, percent	[4] 0.05	[5] 0.21
Octane number	69	73
Octane number+1 cc. T. E. L.	76	78
Octane number+3 cc. T. E. L.	81	81
Hydrogen:		
Hydrogen consumed by sulfur, cu. ft./bbl.	35	30
Hydrogen consumed by olefin, cu. ft./bbl.	310	116
Hydrogen consumed, total cu. ft./bbl.	345	146
Exit hydrogen from plant, cu. ft./bbl.	1,405	1,505

[1] Tetraethyl-lead.
[2] 67% hydrogenation of olefin.
[3] 25% hydrogenation of olefin.
[4] 98% desulfurization.
[5] 82% desulfurization.

Several points can be noted from the above tabulation of data, particularly that it was possible to reduce the sulfur content from 1.17% to 0.21% with only 25% olefin hydrogenation, the octane number being one point higher than in the original charge, possibly due to the removal of sulfur compounds which had a pro-knock tendency, and/or the selective hydrogenation of olefins whose paraffinic counterparts possess high anti-knock value. The sulfur could be reduced to the negligible value of 0.05% with the loss of 3 octane number (72 to 69) with only 67% of olefin hydrogenation. The high susceptibility of the product to tetraethyl lead was also noticeable. In the runs given above the hydrogen excess was approximately 4 times that required for complete saturation of olefins and reduction of sulfur to hydrogen sulfide.

We claim as our invention:

A catalytic hydrogenation process for effecting substantial desulfurization of a gasoline containing both olefinic hydrocarbons and sulfur compounds and hydrogenation of said olefinic hydrocarbons to an extent not materially reducing the anti-knock value of said gasoline, said process comprising subjecting vapors of said gasoline to contact with a nickel sulfide catalyst in the presence of an amount of hydrogen approximately four times that required for complete hydrogenation of said olefinic hydrocarbons and said removal of sulfur and at a temperature of approximately 350° C. under a hydrogen pressure of approximately 900 lbs. per square inch and at a liquid-space velocity of not less than one and not more than two.

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