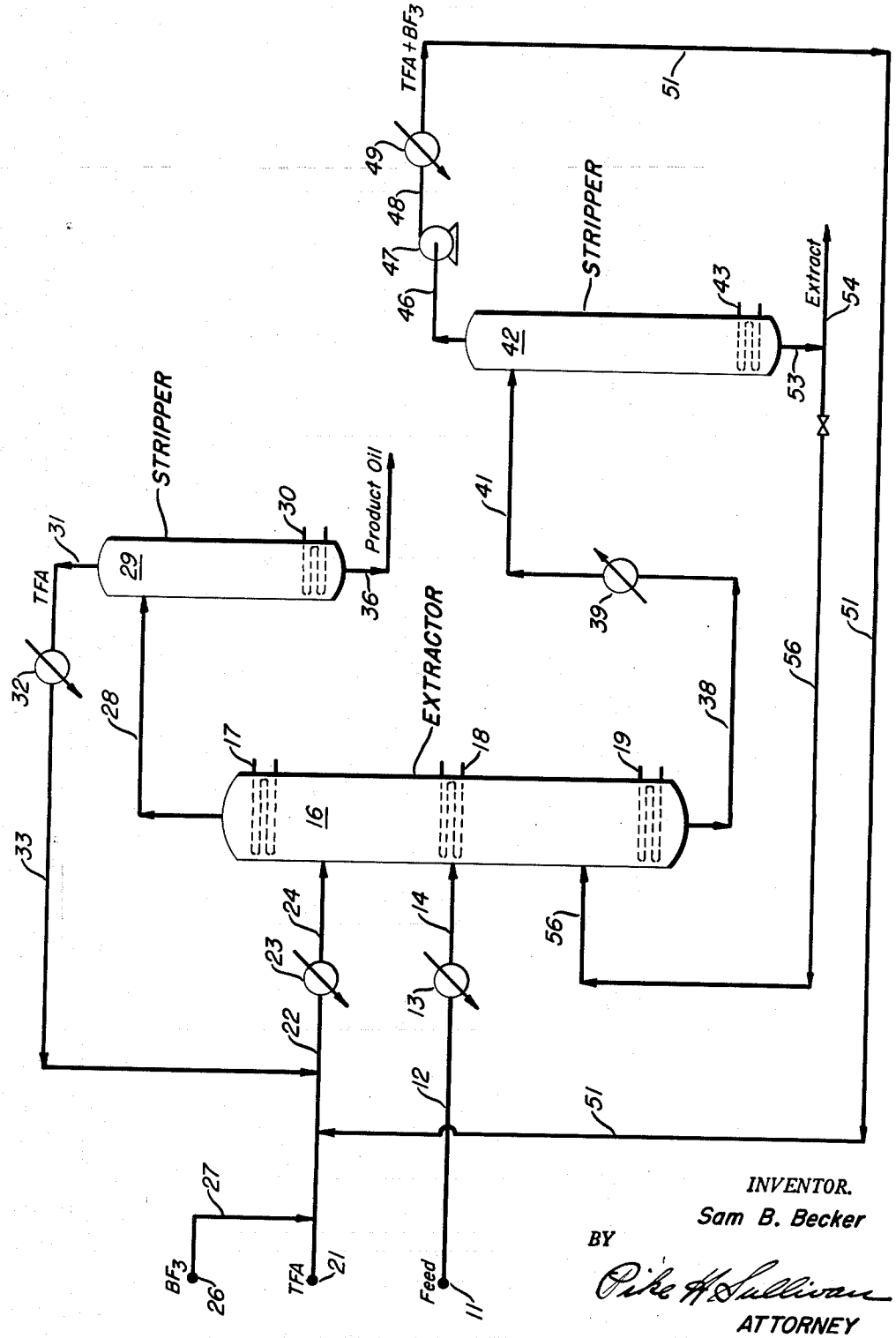
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REFINING HYDROCARBON OILS WITH BF_3 AND PERFLUOROALKANOIC ACID

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REFINING HYDROCARBON OILS WITH BF_3 AND PERFLUOROALKANOIC ACID

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10 Claims. (Cl. 196—31)

This invention relates to the refining of hydrocarbon oils. More particularly, the invention relates to the refining of hydrocarbon oils which contain objectionable amounts of organic sulfur compounds and/or odor bodies and/or other objectionable constituents such as organic nitrogen or oxygen compounds.

Many hydrocarbon oils contain organic sulfur compounds. The presence of these compounds is objectionable because of their adverse effect on odor and their corrosiveness, for some uses. Many oils have objectionable odors even after the sulfur content has been reduced to a relatively low level. A process which selectively removes the organic sulfur compounds and odor bodies is desirable in order to obtain a maximum yield of salable product oil.

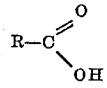
Various oils contain undesirable nitrogen compounds, e. g. shale oils, which also contain organic oxygen and sulfur compounds. Synthetic oils produced by catalytic interaction of carbon monoxide and hydrogen usually contain undesirable organic oxygen compounds.

It is an object of this invention to reduce the organic sulfur content of hydrocarbon oils which contain objectionable amounts of such compounds. Another object is to improve the color and odor of hydrocarbon oils. A particular object is to refine heavy naphthas and oils in the heavier-than-gasoline range by reducing sulfur content and improving color and odor. A further object is to refine hydrocarbon oils containing polar impurities such as organic compounds comprising sulfur and/or oxygen and/or nitrogen and to remove odor and color bodies from such hydrocarbon oils.

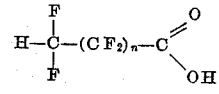
An additional object is to provide a novel composite refining reagent and process to effect the foregoing objects. Yet another object of my invention is to provide novel composite reagents which exhibit unexpected and marked selectivity in combining with polar compounds such as organic sulfur compounds contained in a relatively nonpolar medium such as a hydrocarbon oil and which exhibit said marked selectivity while removing a high proportion of sulfur compounds from said hydrocarbon oil. These and other objects of my invention will be apparent from the ensuing description thereof.

It has been discovered that the color, odor and, particularly, the sulfur content of a hydrocarbon oil, which is unsatisfactory in these respects, are markedly improved by treating said liquid oil with a sufficient amount of a perfluoroalkanoic acid containing two to five carbon atoms, inclusive, in the molecule to form a second liquid phase, and a particular amount of boron trifluoride. The organic sulfur compounds, odor bodies and color bodies pass into the perfluoroalkanoic acid-BF_3 extract phase, leaving a raffinate phase of markedly improved quality.

The perfluoroalkanoic acids employed in practicing the present invention have the general formula



wherein R is an alkyl group of 1–4 carbon atoms in which the hydrogen atoms have been replaced by fluorine atoms. This group of acids includes trifluoroacetic acid (or perfluoroethanoic acid), perfluoropropanoic, n-perfluorobutanoic, perfluoroisobutanoic, n-perfluoropentanoic and perfluoropivalic acids. In addition to, or in lieu of the above-mentioned acids I may use fluoroalkanoic acids wherein departure is made from the fully fluorinated condition only to the extent that an occasional chlorine atom is present in the molecule. Similarly, I may employ acids having the formula



wherein n has an integral value between 1 and 3, inclusive, since the lone hydrogen in the omega position of the alkyl group does not induce chemical properties in the molecule which are substantially different from those of a perfluorinated acid.

Trifluoroacetic acid, hereinafter designated TFA, is a liquid having a specific gravity of 1.535 at 0° C., a melting point of −15° C. and a boiling point of 72.4° C. At temperatures below about 20° C., it is only slightly soluble in higher boiling hydrocarbons. However, it is soluble to the extent of about 20 volume percent in naphthas at about 20° C.

Perfluoroalkanoic acids alone are poor solvents for organic sulfur compounds. Surprisingly enough, TFA is relatively ineffective for the removal of aromatic hydrocarbons from a mixture of aliphatic, naphthenic and aromatic hydrocarbons despite its miscibility with the low boiling aromatic hydrocarbons. The effectiveness of TFA and the other perfluoroalkanoic acids used in the present invention as refining agents (particularly, solvents for organic sulfur compounds) is enormously enhanced by the presence of BF_3. It is believed that a complex reaction occurs between TFA, BF_3 and organic sulfur compounds and the products of this reaction are extremely soluble in the perfluoroalkanoic acids and substantially insoluble in hydrocarbon oils.

The temperature of operation and the particular feed stock have a considerable bearing on the optimum amount of perfluoroalkanoic acid; in general, appreciable refining is obtained by the use of only enough perfluoroalkanoic acid to form a distinct liquid extract phase. The minimum amount of perfluoroalkanoic acid needed is in general between about 10 and 25 volume percent based on oil when operating below about 20° C. The amount of perfluoroalkanoic acid used may be as much as 300% or more. In general, there is no particular gain in desulfurization or other refining action at perfluoroalkanoic acid usage in excess of about 200%. Although the optimum amounts are determined by the feed stock and the temperature of operation, usually proportions between about 25 and 100 volume percent, based on the volume of oil, are employed.

The degree of desulfurization and other refining action obtained is dependent upon the amount of BF_3 present. Hereafter, "mols of BF_3" is intended to mean "mols

of BF_3 per gram atom of sulfur present in the feed"; the same proportions of BF_3 are used with organic oxygen and nitrogen compounds. The amount of BF_3 used may vary from between about 0.1 mols to 6 mols. Usually I use between about 0.5 and 3 mols of BF_3, preferably about 1 mol of BF_3. Although BF_3 is only moderately soluble in perfluoroalkanoic acid under the usual conditions of operation, the desired amount of BF_3 usually can be dissolved by the perfluoroalkanoic acid; in this case, the treating agent will consist of a solution of BF_3 and perfluoroalkanoic acid. Even when the amount of BF_3 used exceeds its solubility in the perfluoroalkanoic acid, the excess BF_3 appears in the extract phase, apparently in the form of an organic complex. The BF_3 may be added to the oil either as a solution in the perfluoroalkanoic acid, may be added to the oil directly or may be pressured directly into the refining equipment.

Water should be rigorously excluded in the present process, viz. from the oils to be refined and from the treating equipment, lines, etc. Water combines with BF_3 to form hydrates which greatly reduce its refining capacity and leads also to increased corrosion of the refining equipment. The oils to be refined can be dehydrated by conventional methods.

The temperature of contacting has a considerable bearing on the effectiveness of the treatment. At temperatures above about 20° C., it is necessary to use large amounts of perfluoroalkanoic acid to obtain phase separation. Usually, refining is effected at temperatures between about +20° C. and −30° C., although even lower temperatures down to about −50° C. may be employed. The treatment of cracked stocks is preferably effected at temperatures between about −10° C. and about −30° C. in order to minimize perfluoroalkanoic acid carry-over into the raffinate phase.

In the treatment of oils of high viscosity or near their freezing point, it is desirable to use a diluent that is inert to the action of BF_3. Suitable diluents are inert hydrocarbons such as propane, butane, hexane, pentane, n-heptane, petroleum ether, naphthenic hydrocarbons, and low boiling aromatic hydrocarbons; I may also employ the corresponding perfluorinated derivatives as diluents. The amount of diluent added will be dependent upon the particular feed stock and operating conditions but, in general, I prefer to minimize the amount of diluent. Usually 10 to 100 volume percent of diluent, based on feed, will be sufficient for satisfactory operation.

The contacting time needed to obtain maximum desulfurization at the particular operating conditions is dependent mainly on the degree of mixing attained. With the normal degree of mixing obtained in commercial contacting apparatus, the contacting time may vary from between about 1 minute and 3 hours. In general a satisfactory degree of refining is obtained when the contacting time is between about 5 and about 30 minutes.

The most common feed stocks charged to the present process are those derived from petroleum, namely, naphthas, kerosene, transformer oil, heater oil, furnace oil, diesel oil and lubricating oil fractions. The present process is especially applicable to virgin distillate heater oils boiling between about 325° F. and 575° F. which contain objectionable amounts of sulfur compounds. In addition to these oils, hydrocarbon oils derived from various conversion processes are a suitable feed to my process. Examples of these are cracked heavy naphtha, cycle stocks from thermal cracking and catalytic cracking operations, coke still naphtha and coke still gas oils. The refining process of the present invention is applicable for the substantial removal of oxygenated organic compounds and nitrogen compounds from hydrocarbon stocks such as Fischer-Tropsch naphthas or diesel oil fractions and from shale oil distillates.

In view of the fact that the present process is selective toward organic sulfur compounds, feed stocks which contain a very high percentage of hydrocarbons, such as benzene, toluene, and xylenes, are a suitable feed to my process. Examples of these stocks are coal tar fractions, coal tar distillates or high aromatic-high sulfur content fractions obtained by the treatment of hydrocarbon oils, such as SO_2 extracts.

In order more fully to describe a specific embodiment of my invention, reference is made to the annexed figure. This embodiment is illustrative only and specifically illustrates the use of TFA–BF_3 although the apparatus and process can be more generally employed in perfluoroalkanoic acid-BF_3 refining. Many variations may be made on the described process by those skilled in the art. All of these variations are intended to come within the scope of the claimed invention.

The feed stock in this embodiment is a virgin heater oil distillate derived from West Texas crude, which oil contains about 0.7 weight percent of sulfur; this feed oil is passed from source **11** through line **12**, exchanger **13** and line **14** into refining and extraction tower **16**. Extraction tower **16** is provided with internal heat exchangers **17**, **18** and **19**, which heat exchangers permit the contents of the tower to be maintained at a substantially constant temperatures, or permit the maintenance of a temperature gradient from top to bottom of the tower. In this embodiment tower **16** is operated at a substantially uniform temperature of about 0° C. Another desirable method of operation involves the employment of a decreasing temperature gradient from the bottom to the top of tower **16**.

While a continuous countercurrent type of operation is shown, the invention is not limited to such operation. A series of batch contacting zones or several towers operated in series may be employed. Series operation with relatively small amounts of BF_3 in each stage effects extensive desulfurization and refining and requires less BF_3 than one-stage operation to achieve the same refining effects. If desired, in a batch process contacting may be effected at a temperature at which one homogeneous phase of acid reagent and hydrocarbon changing stock exist, followed by cooling and/or addition of diluent to effect separation of the homogeneous mixture into a predominantly hydrocarbon (refined) phase and a predominantly acid phase containing sulfur compounds, color bodies, etc. Extraction tower **16** may be packed with suitable corrosion-resistant packing material, such as structural carbon, glass, porcelain, Monel metal, or the like. This packing material should be in the form of Raschig rings, Berl saddles, spheres, etc., or the tower may be provided with mechanically agitated contacting stages.

The process should be operated under substantially anhydrous conditions because of the stability of BF_3 hydrates, resulting in loss of BF_3, and the difficulty of recovering substantially anhydrous TFA. Usually the feed stock will contain so little water that no specific precautions need be taken. However, it may be desirable to provide an electrical, chemical or physical dehydrator to remove water from the feed before the feed passes into extraction tower **16**. A suitable dehydrator is a vessel filled with alumina spheres, glass wool, silica gel or, in some cases, rock salt. Preliminary distillation of the feed stock usually results in its substantial dehydration.

Trifluoroacetic acid from source **21** is passed through line **22**, heat exchanger **23** and line **24** into an upper part of tower **16**. In this embodiment, 50 volume percent of TFA based on the feed, is used. BF_3 from source **26** is passed through line **27** into line **22**, thence into extraction tower **16**. In this illustration, 1 mol of BF_3 per gram atom of sulfur in the feed is used.

A raffinate phase consisting essentially of desulfurized, and substantially mercaptan-free, oil and small proportions of dissolved TFA and BF_3 is passed out of the top of tower **16** through line **28** into stripper **29**. Stripper **29** is provided with internal heater **30**. The temperature in stripper **29** is high enough to distil the dissolved TFA and BF_3. The amount of BF_3 present in the raffinate

phase is very slight because the BF_3 added to the contacting zone is not sufficient to complex all the organic sulfur compounds. The TFA vapors and BF_3 are passed out of stripper **29** through line **31** into cooler **32**; the TFA is condensed in cooler **32** and is passed along with BF_3 by way of line **33** to line **22** for reuse in the process. Provision may be made for intermittent withdrawal of used TFA and BF_3 from the process and their replacement by fresh reagents. A low sulfur, substantially mercaptan-free, good color product oil is withdrawn from stripper **29** by way of line **36**.

From the bottom of extraction tower **16** an extract phase, consisting essentially of TFA, BF_3, organic sulfur compounds, color bodies and some hydrocarbons, is withdrawn through line **38**. The extract phase is passed from line **38** through heater **39** and line **41** into stripper **42**. Stripper **42** is provided with internal heater **43**. In stripper **42** the TFA and BF_3 are withdrawn overhead. The removal of the TFA and BF_3 is facilitated by operating stripper **42** under vacuum. The TFA vapors and BF_3 are passed out of stripper **42** through line **46**, vacuum pump **47** and line **48** into cooler **49**. The TFA is condensed in cooler **49** and the resulting TFA-BF_3 solution is passed by way of line **51** to line **22** for reuse in the process. The bottoms remaining in stripper **42** comprise predominantly organic sulfur compounds, color bodies and odor bodies. The extract is withdrawn from stripper **42** by way of line **53** and is sent to storage not shown by way of line **54**.

The efficiency of operation in extraction tower **16** is markedly improved by the introduction of extract from stripper **42** by way of lines **53** and **56** into a lower portion of tower **16**. This extract functions like reflux in a fractional distillation. When operating with this reflux, sufficient BF_3 must be added to the tower **16** to insure removal of the organic sulfur compounds therein in the extract phase. Operation with a reflux improves the selectivity of operations in the tower with a consequent increase in yield of product oil and no appreciable impairment in the quality thereof.

The above embodiment has illustrated operation on a heavier-than-gasoline boiling range material. When operating on a material, such as a virgin heavy naphtha, in which the TFA is moderately soluble at about 0° C., it is desirable to change the operational features somewhat. Thus when operating on a virgin heavy naphtha, extraction tower **16** is operated at about 0° C.; but the raffinate phase is passed through a cooler which lowers the temperature of the raffinate phase to about −20° C. The cold material is passed from the cooler to a separator in which there separates a second raffinate phase containing only a moderate amount of TFA and a second extract phase consisting essentially of TFA and dissolved BF_3. The second raffinate phase is passed to a stripping operation such as described above. The second extract phase is returned to line **22** for reuse in the process. This separation-by-cooling method is particularly desirable when the lower boiling constituents of the feed have about the same or only a slightly higher boiling point than TFA. Similar results can be obtained by cooling the upper portion of tower **16** by means of heat exchanger **17**.

The following specific examples are intended to be illustrative of the results obtained by my process; but are not to be considered as limiting the scope of my invention. The extractions were carried out in a stainless steel bomb which was maintained at the desired temperature of contacting by immersion in a naphtha Dry Ice bath. A fixed amount of the particular feed oil was added to the bomb and then the desired amount of TFA was added to the bomb. The bomb and its contents were then brought to the desired temperature. The desired amount of BF_3 was metered into the bomb. The bomb was shaken vigorously for about 5 minutes and then the contents were allowed to settle for about 10 minutes. After the settling period the two phases were withdrawn separately. In all the

runs excellent phase separation was obtained. The raffinate phase was washed with water and with dilute aqueous caustic to remove dissolved TFA and BF_3. The TFA and BF_3 were removed from the extract phase by distillation under vacuum. In all cases extremely good recoveries of the treating agent were obtained. The raffinate oil and the extract oil were analyzed for sulfur content and for aromatic hydrocarbon content.

Four feed stocks derived from West Texas Crude were used in the runs reported hereinbelow. The characteristics of these feed stocks are:

	Gas Oil	Heater Oil	Virgin Naphtha	Cracked Naphtha
Sulfur, Wt. Percent	1.5	0.7	0.32	0.29
°API	31.5	40.9	55.2	55.4
Refractive Index, n_D^{20}	1.4825	1.4558	1.4239	
ASTM Distillation, ° F.:				
IBP	432	330	132	140
50%	574	450	265	260
Max	650	555	402	405

The results of the various runs are listed below.

Run	Feed	TFA, Vol. Percent	BF_3 Mols/g. Atom S	Temp., ° C.	Raffinate [1]		Desulfurization, Percent
					Percent Sulfur	Yield, V. percent	
1	G. O.	100	None	+20	1.34	96	11
2	G. O.	100	1	+20	0.70	90	54
3	G. O.	50	2	+20	0.8	92	46
4	G. O.	50	2	0	0.8	93	46
5	H. O.	50	None	−20	0.55	96	25
6	H. O.	None	1	−20	0.58	99	17
7	H. O.	50	1	−20	0.21	95	71
8	V. N.	100	2	−20	[2] 0.07	90	78
9	V. N.	50	2	−20	[2] 0.07	90	78
10	C. N.	100	1	−20	[2] 0.10	90	66

[1] In all cases except Runs 1, 5 and 6 the color and odor were very much improved over the feed.
[2] Sweet by the doctor test.

Runs 1, 5 and 6 show that little improvement in sulfur content is obtainable when using TFA or BF_3 alone. Even if the improvement by BF_3 treatment alone and TFA alone are added, Run 2 shows a remarkable increase in desulfurization ability for the TFA-BF_3 treatment of gas oil. Similarly Run 7 shows a remarkable increase for the TFA-BF_3 treatment of heater oil. Cracked naphthas are notoriously difficult to desulfurize, the 66% desulfurization achieved in Run 10 is astounding.

In the following examples n-perfluorobutanoic acid was employed. This acid had a normal boiling point of 120° C., freezing point of 17.5° C. and d_4^{25} of 1.641. A West Texas heater oil containing color bodies, odor bodies and a total sulfur content of 0.607 weight percent was refined. The oil was added to the perfluorobutanoic acid in a stainless steel bomb at the desired temperature and BF_3 was then pressured into the bomb. The bomb was shaken vigorously for 2 minutes and the contents were then allowed to settle for 10 minutes or more. The phase separation between the liquid raffinate and the liquid extract layer was sharp. The lower (extract) layer was drawn off. The upper (raffinate) layer was washed twice with 10 ml. portions of water, once with dilute caustic, and once more with water. The initial water washes removed substantially all the perfluorobutantoic acid. The washed raffinate was filtered through filter paper and its sulfur content was determined. In the treatments of this West Texas heater oil with 50 volume percent perfluorobutanoic acid at 25° C. it was found that less than 4% of said acid remained in the raffinate phase immediately after extraction. The selectivity of the BF_3-perfluorobutanoic acid reagent is clearly illustrated by the fact that under the above-mentioned conditions, less than 5 volume percent of the heater oil was dissolved in the extract phase, although great improvements in color and odor of the raffiate oil were effected, together with a

very substantial decrease in the sulfur content thereof. The following data were obtained:

Run No.	11	12	13
Charge:			
Perfluorobutanoic acid (ml.)	10	25	25
West Texas Heater Oil (ml.)	30	50	50
BF_3 (mols per mol sulfur)	0	ca. 1	ca. 2
Conditions:			
Contact time (min.)	2	2	2
Temperature, °C.	25	25	10
Analysis, w. percent:			
Sulfur in untreated oil	.607	.607	.607
Sulfur in treated oil	.571	.357	.352
Sulfur removal	.036	.250	.255
Percent of total sulfur removal by extraction	6	41	42

It will be noted that in Run 11 only very slight refining of the oil occurred as evidenced by mineral desulfurization. In contrast are the results obtained in Runs 12 and 13 wherein not only substantial desulfurization was obtained but a great decrease in color bodies and great improvement in the odor of the treated oil. It will further be noted from a comparison of Run 13 with Run 12 that no substantial advantage accrued to the employment of the larger proportion of BF_3.

This application is a continuation-in-part of my application for United States Letters Patent, Serial No. 275,092, filed March 6, 1952, now abandoned.

Having thus decribed my invention, what I claim is:

1. The method of refining a sulfur-containing hydrocarbon oil and simultaneously improving the odor and color of said oil, which method comprises contacting a substantially dry sulfur-containing oil with about 10 to 300 volume per cent based on oil of a perfluoroalkanoic acid having at least 2 but not more than 5 carbon atoms per molecule in the presence of about .1 to 6 mols of BF_3 per gram atom of sulfur present in the oil at a temperature in the range of —50° C. to the miscibility temperature of the mixture to effect substantial desulfurization of said oil, removing from the mixture two separate liquid phases at a temperature low enough to provide a perfluoroalkanoic acid-BF_3 phase containing only a minor amount of the oil charged and a hydrocarbon phase containing most of the oil charged, removing perfluoroalkanoic acid and BF_3 from the perfluoroalkanoic acid-BF_3 phase and separately removing dissolved extractant material from the hydrocarbon phase to obtain a desulfurized product oil of improved odor and color.

2. The method of claim 1 wherein said oil is a virgin naphtha.

3. The method of claim 1 wherein said oil is a cracked naphtha.

4. The method of claim 1 wherein said oil is a gas oil.

5. The method of claim 1 wherein said oil is a virgin heater oil.

6. The method of claim 1 wherein said oil is a diesel oil.

7. The method of claim 1 in which the contacting is effected at a temperature in the range of about —30° to about +20° C.

8. The method of claim 1 wherein the perfluoroalkanoic acid is present in an amount between about 25 and 100 volume per cent based on said oil and BF_3 is present in amount between about 0.5 and 3 mols per gram atom of sulfur in said oil.

9. The method of claim 1 wherein the perfluoroalkanoic acid is trifluoroacetic acid.

10. The method of claim 1 wherein the perfluoroalkanoic acid is perfluorobutanoic acid.

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