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NITROGEN-CONTAINING OXIDIZED OIL PRODUCTS AND FUEL AND LUBRICATING OIL COMPOSITIONS CONTAINING THE SAME

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This invention relates broadly to the oxidation of lubricating oils. More particularly, it relates to the oxidation of lubricating oils in the presence of ammonia to form nitrogen-containing oxidized oil products which are useful as addition agents for hydrocarbon lubricating oils and fuels.

It has been known heretofore to oxidize hydrocarbon oils with air in the presence of metallic bases whereby the products produced are metal salts of the oxidized oil. These metal salts have proved highly useful as additives for petroleum products, particularly as detergents or dispersing agents in crankcase lubricating oils. In modern automotive engines, however, combustion chamber deposits have reduced performance efficiency. Thus, phenomena, such as pre-ignition, spark plug fouling, wild ping, etc., have been found to be caused by metallic ash deposits which are formed, partly at least, from the metal-containing detergent additives used in the lube oils. In an effort to reduce these deposits and alleviate these problems, the art has turned to the development of "ashless" (i.e., non-metal containing) detergents as replacements for the metal-containing detergents. The products provided by the present invention have been found to be excellent ashless detergents for automotive oils. Furthermore, these products have been found to be highly effective additives for fuel oils and gasolines. Thus, they provide excellent anti-clogging properties in fuel oil and are effective anti-icing agents for gasoline. As far as is known, products of the type provided by the invention have not been made heretofore and they are, therefore, considered to be new compositions of matter. Accordingly, it is the primary object of this invention to provide a new class of nitrogen-containing oxidized oil products.

It is a further object to provide a method for the preparation of these new nitrogen-containing oxidized oil products. It is another object to provide lubricating oil compositions containing these products as ashless detergents. It is a still further object to provide fuel oils containing these products, said oils having improved anti-clogging properties. It is also an object to provide gasoline compositions containing these products which exhibit improved anti-icing properties.

In accordance with the invention, the nitrogen-containing products thereof are prepared by the method which comprises oxidizing a hydrocarbon oil with a free-oxygen containing gas, such as air or oxygen, in the presence of ammonia. The process is carried out by heating the oil to a temperature of, say, 200° F. to 500° F. and then passing air or oxygen and ammonia simultaneously through the heated oil. This treatment is continued for a time sufficient to incorporate from about 0.1% to 1.2% nitrogen into the oxidized oil. The treated oil is then filtered to remove insolubles.

It will be appreciated that the time required to attain the required level of nitrogen content in the treated oil will vary in accordance with the conditions used, such as the heating temperature, the rate of introduction of the air and ammonia and the efficiency of the contacting of these gases with the oil. In all, except one, of the examples presented hereinafter, the process was conducted

in an electrically heated upright glass cylinder, 60 inches long and 3 inches in diameter, equipped with a fritted glass gas disperser at the bottom thereof. In the one example, it was conducted in a 3-liter, round-bottomed flask equipped with a stirrer and two filter sticks for the air-ammonia dispersion and a temperature regulator. Using these reactors and employing a heating temperature of 400° F., an air introduction rate of 2 to 3 liters per hour per 100 grams of oil and an ammonia introduction rate of 0.3 to 0.65 liter per hour per 100 grams of oil, treating times of from about 6 to 25 hours were required to provide the desired level of nitrogen content in the treated oil.

However, it will be appreciated that these conditions will not necessarily hold true when reactors different from those employed in the examples are used. Thus, in operating the process on a commercial scale, it would be expected that reactors designed to give a more efficient dispersal of the air and ammonia through the oil will be employed and, therefore, much shorter reaction times attained. Likewise, the efficiency of the process could be increased by the use of specially designed pressure reactors. It will be understood that using such reactors the rates of introduction of the reactant gases could vary considerably from those shown in the examples. It will be appreciated, therefore, that the time for completing the process is not subject to numerical definition, but is dependent upon the equipment and other conditions used. The time for completing the process is, therefore, expressed herein as that sufficient to incorporate the required nitrogen content, i.e., from 0.1% to 1.2% in the treated oil product.

From the standpoint of efficiency and economy, experience has shown that the (volume) ratio of the air to ammonia charged to the oil should be at least about 1:1 and preferably higher. From the examples, it will be seen that ratios of 3:1 and 10:1 show no appreciable difference in the results obtained, and ratios as high as about 20:1 are considered practical. On the other hand, it has been found that the use of air to ammonia ratios less than 1:1 results in unfeasible low yields of the nitrogen-containing products. It will be appreciated that if oxygen is utilized in the process as the oxidizing gas rather than air the proportion of oxygen required will be only about one-fifth that of air. Thus, the oxygen to ammonia ratio ranges from about 0.2:1 to about 4:1.

The precise nature of the nitrogen-containing products formed in the process of the invention is not known. Theoretically, a variety of organic nitrogenous compounds can be formed in the process. Analytical data show that, besides containing nitrogen, the processed oil also contains substantial amounts of oxygen, i.e., from about 1.5 to about 3.0 weight percent, and that the higher nitrogen-content products generally exhibit the highest oxygen contents. Also, perchloric acid titration has shown that about 70% to about 80% of the nitrogen-containing components are non-basic compounds. Without intending to limit the invention by theoretical considerations, it is believed that these non-basic components may be complex high molecular weight compounds involving pyrimidine, pyrazine, pyrrole, etc., as parent nuclei.

The process of the invention can be applied to all types of lubricating oil stocks, ranging from relatively light stocks having average molecular weights of about 300 up to heavy lube oil stocks having molecular weights of about 1000. The properties of several different types of suitable stocks are given in Table I.

TABLE I.—PHYSICAL PROPERTIES OF HYDROCARBON OIL STOCKS

Stock	Gravity, °API	K.V. at 210° F., cs.	Average Molecular Weight
Mid-Continent Bright (330)	25.8	25.9	720
Mid-Continent Bright (345)	26.3	32.9	840
East Texas Heavy Waxy Distillate (399)	28.9	9.3	500
300" Mid-Continent Paraffin Oil	25.0	7.7	300-400
Residue from Dodecyl Benzene Production [1]	29.0	6.92	320

[1] A high-boiling hydrocarbon fraction obtained as a by-product in the manufacture of dodecyl benzene composed predominantly of alkyl aromatics (60-80 weight percent), the remainder being non-aromatics. This particular fraction had a boiling range of 592-828° F., an API Gravity of 292 and a Flash Point of 370° F. These properties, which are typical of such a by-product fraction, may vary somewhat from batch to batch without effecting the utility of this material in the invention.

A series of examples, 1–11, illustrating the process of the invention are summarized in Table II. Typical of these examples is Example 1, set forth herebelow.

Example 1.—Two thousand grams of a Mid-Continent type bright stock were charged to an electrically heated glass column (60" long and 3" diameter) equipped with a gas disperser in the bottom. Streams of air and ammonia at rates of 3.0 l./hr./100 g. oil and 0.3 l./hr./100 g. oil, respectively, were passed simultaneously through the oil heated at 400° F. for 13 hours. The finished product was filtered. Analysis showed the nitrogen content of the product to be 0.48%.

splash lubrication is used. The operating conditions are as follows:

Oil temperature	° F.	225
Jacket temperature	° F.	275
Speed	r.p.m.	1825
Brake load	H.P.	1.6

One-half throttle.
13–1 air-fuel ratio.
Oil added every 20 hours (one gallon sample used).

The duration of the test is 100 hours. The fuel used is a premium type gasoline composed of 40% thermal, 30% catalytically cracked and 30% straight-run components plus 2.5 cc. TEL/gal.

CFR Diesel Detergency Test

This test determines the effectiveness of the lubricating oil in preventing piston deposits and top ring wear. A single cylinder CFR, 4-cycle, super-charged, diesel engine is used. The operating conditions are as follows:

Oil temperature	° F.	175
Jacket temperature	° F.	215
Speed	r.p.m.	1825
Brake load	H.P.	7.5
Oil addition every 8 hours starting at 4 hours (1½ gallon sample used).		
Heat input	B.t.u./min.	1260

The duration of the test is 60 hours. The fuel used is a No. 2 fuel oil containing 1% sulfur. The results are reported in terms of piston cleanliness ratings as in the Lauson test.

TABLE II.—OXIDATION OF HYDROCARBONS IN THE PRESENCE OF AMMONIA

Example	Charge Stock [a] Type	Grams	Air Rate, l./hr./100 g.	NH_3, l./hr./100 g.	Temp., ° F.	Time, Hr.	Percent Nitrogen		Percent Oxygen
							Total	Basic	
1	Mid-Cont. 330 Bright	2,000	2.0	0.65	400	9	0.28		
						13	0.48	0.15	
2	do	2,000	2.0	0.65	400	24	1.18	0.62	
3	Mid-Cont.[b] 330 Bright	1,000	2.0	0.5	424	26	0.87	0.21	
4	Mid-Cont. 330 Bright	2,000	3.0	0.3	400	13	0.57		2.31
5	do	2,000	3.0	0.3	400	13	0.61		
6	Mid-Cont. 345 Bright	2,000	3.0	0.3	400	6.5	0.19		1.65
7	do	2,000	3.0	0.3	400	14.0	0.56		2.20
8	do	2,000	3.0	0.3	400	21.0	1.05		2.75
9	399 Hvy Waxy Distillate	2,000	2.0	0.65	400	20.0	0.58		
10	300 Scc. Mid-Cont. Paraffin Oil	2,000	3.0	0.3	400	9.0	0.33	0.06	
11	Residue from Dodecyl Benzene Production.[c]	2,000	3.0	0.3	400	7.0	0.30		
						14.0	0.55		
						21.0	0.75		

[a] The oxidation reaction was carried out, except where noted, in an electrically heated glass column (60" l. x 3" d.) equipped with a fritted glass disperser in bottom.
[b] The oxidation reaction was carried out in a 3 l. round bottom flask equipped with a stirrer, two filter sticks (for air-ammonia dispersion) and a temperature regulator.
[c] Properties are given in Table I (supra).

Evaluation of Products

(a) AS LUBRICATING OIL DETERGENTS

The ability of the products of the invention as "ashless" detergents for engine lubricating oils has been demonstrated by comparative tests conducted on the base lubricating oil and on the base oil blended with minor amounts of representative products. The tests used were the Lauson detergency test and the CFR diesel detergency test. The results of these tests are presented in Table III. The test procedures were as follows:

Lauson Detergency Test

This test determines the effectiveness of the lubricating oil in preventing fouling as measured by the cleanliness of rings, lands, ring grooves and piston skirts. Cleanliness ratings are based on a scale of from 100 to 0, a 100 rating signifying a perfectly clean condition and a 0 rating representing the worst possible deposit condition. A single cylinder, 4-cycle, liquid-cooled Lauson engine with

TABLE III

Product Added	Percent Product In Oil	Lauson Detergency Test Rating [a]	Diesel Detergency Test Rating [b]
None		59	62
Ex. 1	6		76
Ex. 1	12		85
Ex. 3	6	73	64
Ex. 3	6	68	

[a] The base oil is an SAE 20 Grade solvent refined Penna. oil (K.V. at 100° F.=63 cs.; K.V. at 210° F.=8.3 cs.) containing 1.0% of a commercial anti-oxidant (Pinene-P_2S_5 product).
[b] The base oil is an SAE 30 Grade solvent refined Mid-Continent oil (K.V. at 100° F.=121 cs.; K.V. at 210° F.=12.2 cs.) containing 1.0% of a commercial anti-oxidant (Pinene-P_2S_5 product).

It will be seen from Table III that the products of the invention are effective detergents for engine oils.

(b) AS AN ANTI-CLOGGING ADDITIVE IN FUEL OIL

As is well known, fuel oils, particularly distillate fuel

oils, such as those used as domestic heating oils and diesel fuels have a tendency to deteriorate in storage and form sludge. Also, by the time the fuel oil reaches the consumer it contains small amounts of foreign substances, such as condensed moisture, and particles of rust and dirt, which become entrained in the oil from the tanks, pipes, etc., of the fuel distribution system. A serious problem encountered with fuel oils arises from their tendency to deposit the formed sludge and foreign bodies on the screens, filters, nozzles, etc., of burners and engines using them. These deposits cause clogging of these elements which in turn necessitates cleaning and repair costs. The art has found that this clogging problem can be substantially alleviated by the addition to the fuel oil of minor amounts of chemical additives known as anti-clogging agents, which have the ability to prevent these deposits. The products of the present invention have been found to exhibit excellent anti-clogging action when added to fuel oils, as shown by a series of anti-screen clogging tests, the results of which are presented in Table IV below.

The test procedure involved pumping a fuel oil contaminated with 15 grams per 4 liters of a synthetic sludge, composed of 10% carbon, 50% water and 40% fuel oil, through a conventional oil burner screen for two hours. The amount of deposits on the screen at the end of the test is rated on a scale of from 100 to 0, a rating of 100 indicating a perfectly clean screen and a rating of zero representing the sludge deposited by the base fuel containing no additive. The base fuel oil used in the tests comprised 60% catalytically cracked component and 40% straight-run components and had a boiling range of approximately 320° F. to 640° F.

TABLE IV

Product Added To Fuel Oil	Percent Nitrogen	Screen-Clogging Test Rating		
		25#/MB	50#/MB	100#/MB
None		0	0	0
2	1.18	66	78	96
3	0.87	98	98	99
5	0.61	84	96	98
6	0.19	0	10	29
7	0.56	44	96	99
8	1.05	97	98	97
11	0.55	41	35	50

It will be seen from Table IV that all of the products of the invention exhibited anti-clogging ability, the higher nitrogen-content products being generally more effective than those of lower nitrogen content. Also, the products prepared from residual or bright stocks appear to be more effective than those from lighter stocks (compare Examples 7 and 11).

(c) AS A GASOLINE DETERGENT ADDITIVE

With the coming of the modern high compression gasoline engine, fuel as well as lubricating oil problems have arisen. In the case of fuel, one of the main problems in engines has been the development of manifold, valve and piston deposits. To decrease the amount of these deposits, refineries have resorted to additives. The nitrogen-containing products of the present invention have been found to be effective for inhibiting these deposits in low and high temperature operated engines, as shown by the following tests, the results of which are presented in Table V.

The tests used where the FL–2 Chevrolet Engine (low temperature) Test and the L–4 Chevrolet Engine (high temperature) Test. The base gasoline employed in the FL–2 test comprised 92% thermal reformate and 8% heavy naphtha plus 2.5 cc. TEL. In the L–4 test the base gasoline used was a 50/50 blend of thermal reformate and heavy naphtha containing 3.0 cc. of TEL. The crankcase oil used in both tests was an SAE 30 grade oil (K.V. at 210° F.=11 cs.) fortified with 3% of a commercial detergent and 1.75% of a combination of commercial anti-oxidant additives.

FL–2 Chevrolet Engine Test

This test determines the effect of fuels on the formation of engine deposits at low operating temperatures. In this test a standard six cylinder Chevrolet passenger car engine is operated under the following conditions:

Oil temperature	155° F.
Jacket inlet	85° F.
Jacket outlet	95° F.
Speed	2500 r.p.m.
Brake load	4.5 H.P.
Oil addition	Level adjusted every 10 hours.

The duration of the test is 40 hours. The overall engine rating is obtained from inspection of the various parts of the engine for varnish and sludge deposits. The ratings are based on a scale of from 100 to 0, 100 indicating a perfectly clean engine, while 0 would indicate the worst possible deposit condition. The pistons and inlet valves were also rated on a scale of from 10 to 0, a rating of 10 indicating a perfectly clean condition.

L–4 Chevrolet Engine Test

This test determines the effect of fuels on the formation of engine deposits at low operating temperatures. In this test a standard six cylinder Chevrolet passenger car engine is operated under the following conditions:

Oil temperature	280° F.
Jacket temperature	200° F.
Speed	3150 r.p.m.
Brake load	30 H.P.
Oil addition	Level adjusted every 4 hours.

The duration of the test is 36 hours. At the completion of the test the engine is dismantled and inspected and cleanliness ratings made in the same manner as in the case of the FL–2 test (supra).

The results obtained in the several tests are given in Table V.

TABLE V.—GASOLINE DETERGENCY TESTS

	FL–2 Chevrolet		L–4 Chevrolet	
	Base Fuel	Base Fuel +0.12% Ex. 5 Product	Base Fuel	Base Fuel +0.12% Ex. 5 Product
Piston Rating	5.5	8.2	9.3	9.5
Inlet Valve Rating	7	8	7+	8+
Overall Rating	86	89	95	94

From Table V, it is seen that when added to the gasoline at 0.12%, by weight, concentration, the additive effected a marked reduction in piston deposits over that obtained with the base fuel in the FL–2 test. Also, it is seen that the inlet valve ratings were improved in both tests. Furthermore, in both tests the good overall engine cleanliness rating, attributable to the detergent-anti-oxidant lubricating oil used, was not effected.

(d) AS A GASOLINE ANTI-STALLING AGENT

A well known difficulty encountered in the operation of automobile engines in cool and humid weather is that of frequent stalling during the warm-up period. It has now been recognized that the cause of this stalling is ice formation in the carburetor. The trouble has become more prevalent in post-war cars since the use of automatic transmissions and automatic chokes and the elimination of the hand throttle gives the driver less control over the engine during warm-up. In addition to the inconvenience of restarting, this type of stalling is a serious safety hazard. The stalling mechanism is generally

agreed to be as follows: As the fuel evaporates, it removes heat from the surrounding metal parts thereby lowering their temperature. The temperature is quickly lowered below 32° F. if the ambient temperature is low enough and the fuel is sufficiently volatile. Moisture in the incoming air that comes in contact with these cold parts begins to form a coating of ice. The ice first appears on the throttle plate and carburetor barrel near it. If enough moisture is present in the incoming air, the ice continues to build up on the top and edges of the throttle plate. When the throttle plate is closed, as during idling, the ice chokes off the air flow through the small clearance between the plate and carburetor wall. This causes the engine to stall. The engine can usually be restarted since heat from the exhaust manifold melts the ice. However, stalling will continue until the engine is warmed up. This may require 10 to 20 minutes under severe conditions. Atmospheric conditions conductive to stalling are ambient temperatures of 30° F. to 60° F. and relative humidity above 65%. The most critical conditions are 35° F. to 40° F. ambient temperature at 100% relative humidity.

The nitrogen-containing oxidized oil products of the present invention have been found to be effective anti-stalling agents for gasolines as shown in the following tests. The base fuel used in these tests was comprised of 68% catalytically cracked gasoline, 9% natural gasoline, 8% benzene, 12% toluene and 3% butene. It had a boiling range of 97° F. to 382° F.

The test procedure used was as follows: A standard Chevrolet engine, equipped with a Holley single downdraft carburetor, was mounted in a "cold" room in which the temperature was maintained at 50° F. The Holley carburetor was used because it has been shown to be very susceptible to icing. A thermo-couple was attached to the throttle plate shaft to record the plate temperature. A ½-inch insulating gasket was placed between the carburetor and manifold to prevent heat conduction. An asbestos sheet covered the entire manifold system to shield the carburetor from convection and radiation. A spray chamber was used to saturate the incoming air with moisture before entering an ice tower which cooled the air to about 35° F.

In conducting a test, the engine was first run for about 10 minutes at 2500 r.p.m. to bring the engine temperature to equilibrium. The engine was then shut off. When the throttle shaft temperature rose to 40° F., the engine was restarted and run for a period of from 20 to 60 seconds at 2500 r.p.m. At the end of the selected run-time, the throttle arm was moved to the idle position, which was set at 450 r.p.m. The time required to stall was recorded. Several tests were made at each run-time and averaged.

In evaluating an additive, the base fuel was first tested and subsequent tests were made on blends of the additive in the base fuel. The system was flushed between tests with the fuel to be run next. Any anti-icing improvement effected by the additive was reflected by a longer time to stall at idle as compared to the base fuel. The test results are presented in Table VI.

TABLE VI.—ANTI-STALLING TESTS

Run Time at 2500 r.p.m. (Sec.)	Idling Time (Sec.) to Stall (450 r.p.m.)		
	Base Fuel	Base Fuel +0.01% Product of Ex. 5	Base Fuel +0.05% Product of Ex. 5
20	>60	>60	>60
30	>60	>60	>60
40	4	>60	>60
50	0	>60	>60
60	0	9	>60

It will be seen from Table VI that the product of Example 5, which is typical of the products of the invention, is an effective anti-icing agent for motor gasoline. Thus, it is seen that at run-times sufficient to permit ice formation in the carburetor stalling was encountered in the absence of the additive. Thus, when operated on the base gasoline, the engine stalled in 4 seconds at 40 seconds run-time and immediately at 50 and 60 seconds run-time. However, when operated on the gasoline containing the additive the stalling time was extended to over 60 seconds at 40 and 50 seconds run-time at the 0.01% additive level. Also, at 60 seconds run-time, the stalling time was extended to 9 seconds by the use of 0.01% of the additive and again to over 60 seconds by the use of 0.05% of the additive.

When utilized as "ashless" detergents the products of the invention may be added to a lubricating oil in amounts ranging from about 1.0% to as high as about 20%, by weight, depending upon the requirements of the oil and the application for which it is intended, the usual amount being from about 3% to about 10%. Much smaller amounts are required, however, when the products are employed as anti-clogging agents in fuel oils. Thus, for this purpose the additives are added to the fuel oil in amounts ranging from about 10 to about 200 pounds per 1000 barrels of the oil, i.e., from about 0.003% to about 0.06%, by weight. As anti-stall additives for gasoline, the required amounts are also quite small, ranging from about 0.01% to about 0.1%, by weight.

It will be appreciated that the products of the invention are actually dilute oil solutions of the nitrogenous compounds formed by the air-ammonia treatment. Accordingly, it is considered feasible to concentrate these solutions, i.e., increase the proportion of the nitrogenous products therein prior to the use thereof as oil additives. Thus, as those skilled in the art will appreciate, this can be accomplished by known techniques, such as solvent-extraction, distillation, chromatographic absorption, etc. It will be understood, however, that if such concentrating techniques are applied to the products of the process, the amounts thereof required for use as additives in lubricating oils and fuels will be proportionately less than those recited hereinabove for the unconcentrated products.

It will be appreciated, furthermore, that manufacture of the products of the invention on a commercial basis would involve standardization of process conditions and/or final adjustment of the concentration of the nitrogen-containing compounds in the product oil solution to some standard level so as to insure uniformity of the products.

It will be understood that in addition to the products of the pesrent invention, lubricating oils, fuel oils and gasolines may have added thereto other additives designed to improve the properties thereof in various respects. Thus, lubricating oils may contain anti-oxidants, pour point depressants, viscosity index improvers, extreme, pressure agents, anti-rust agents, etc., as well as other detergents. Likewise, fuel oils can contain anti-oxidants, burning and ignition quality improvers, foam inhibitors, anti-rust agents, etc. Similarly, gasolines may also contain anti-knock agents, rust inhibitors, metal deactivators, etc.

Although the principles of this invention have been illustrated herein by means of certain specific examples and tests, it is not intended that the scope of the invention be limited thereby, but only as indicated in the following claims.

What is claimed is:

1. As a new composition of matter, a nitrogen-containing oxidized mineral oil product produced by the method which comprises heating a mineral oil to a temperature of from about 200° F. to about 500° F., simultaneously introducing air and ammonia gas into the

heated oil in a volume ratio of from about 1:1 to about 20:1, for a time sufficient to incorporate into the oil from about 0.1% to about 1.2%, by weight, of nitrogen and filtering the treated oil.

2. A method for producing a nitrogen-containing oxidized mineral oil product which comprises heating the mineral oil to a temperature of from about 200° F. to about 500° F., simultaneously introducing air and ammonia gas into the heated oil in a volume ratio of from about 1:1 to about 20:1, for a time sufficient to incorporate into the oil from about 0.1% to about 1.2%, by weight, of nitorgen and filtering the treated oil.

3. A method for producing a nitrogen-containing oxidized mineral oil product which comprises heating the mineral oil to a temperature of from about 200° F. to about 500° F., simultaneously introducing (*a*) a free oxygen-containing gas, selected from the group consisting of oxygen and air and (*b*) ammonia gas, into the heated oil, the volume ratio of said oxidizing gas to ammonia so introduced being from about 0.2:1 to about 4:1 when said free oxygen-containing gas is oxygen and from about 1:1 to about 20:1 when said free oxygen-containing gas is air, for a time sufficient to incorporate into the oil from about 0.1% to about 1.2%, by weight, of nitrogen and filtering the treated oil.

4. A mineral lubricating oil, containing a minor amount, sufficient to improve the detergent characteristics of said oil, of a nitrogen-containing oxidized mineral oil product produced by the method which comprises heating a mineral oil to a temperature of from about 200° F. to about 500° F., simultaneously introducing air and ammonia gas into the heated oil in a volume ratio of from about 1:1 to about 20:1, for a time sufficient to incorporate into the oil from about 0.1% to about 1.2%, by weight, of nitrogen and filtering the treated oil.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Henry G. Berger et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 3 and 4, TABLE II, under the heading "Percent Nitrogen", sub-heading "Basic", line 3 thereof, for "0.62" read -- 0.26 --; column 8, line 54, for "pesrent" read -- present --; column 9, line 12, for "nitorgen" read -- nitrogen --.

Signed and sealed this 1st day of December 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
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Commissioner of Patents