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[54] **SULFURIZATION OF TRIISOBUTYLENE AND PRODUCTS RESULTING THEREFROM**

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[58] **Field of Search** 252/45

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[57] **ABSTRACT**

A process for the sulfurization of triisobutylene and resulting products comprising contacting triisobutylene with sulfur under essentially atmospheric conditions at a temperature between about 360° and 500°F., utilizing a mole ratio of triisobutylene to sulfur of between about 1:4 and 1:2.5 while blowing the reaction mixture during at least a part of said contacting with an inert gas and recovering a sulfurized triisobutylene product containing as a major component a compound of the empirical formula $C_{12}H_{20}S_3$ having substantially reduced corrosive activity to copper coupled with superior EP (extreme pressure) improving properties when incorporated in hydrocarbon lubricating oils such as gear oils and cutting oils.

3 Claims, No Drawings

SULFURIZATION OF TRIISOBUTYLENE AND PRODUCTS RESULTING THEREFROM

BACKGROUND OF INVENTION

Sulfurized isobutylene and polyisobutylene such as di- and triisobutylene have long been known as additives for lubricating oils. They are in reality a complex mixture of products theorized to be principally 4,5-dialkyl-1,2-dithiole-3-thione and minor amounts of sulfides, polymeric sulfur substituted compounds and mercaptans. One class of sulfurized olefins and polyolefins has been found to be useful as extreme pressure (EP) agents in lube oils such as gear and cutting oils. These gear and cutting oils may be further described as paraffinic and naphthenic oils having an SUS viscosity at 100° F. between about 100 and 2,500. In order for the sulfurized polyolefin to effectively function as an EP additive agent, the sulfur therein should be in a chemically active state, as opposed to an inactive state. The inactive sulfurized olefins are primarily employed in automotive crankcases as antioxidant additives, particularly where the metals coming in contact therewith are highly sensitive to corrosion, and therefore, could not tolerate active sulfur.

One of the continuing problems in the sulfurized olefinic extreme pressure agent field is to produce a sulfurized polyolefin which has sufficiently active sulfur to satisfactorily function as an extreme pressure agent, and yet, remain relatively insensitive to copper, e.g., of a copper corrosion strip rating of less than about 4A (3hr./250° F.) at concentrations of about 1 wt. %. The Copper Strip Test (ASTM D130-68) is a measure of the corrosivity of the additive to its metallic environment particularly copper.

In one past procedure in order to reduce the Copper Strip rating, triisobutylene and sulfur were reacted utilizing a 5 wt. % stoichiometric excess of triisobutylene (assuming the stoichiometric mole ratio of olefin to sulfur is 1:5) under atmospheric pressure, filtering the resultant product, and then washing the resultant product with an aqueous solution of sodium sulfide. The sodium sulfide treatment apparently removes those active sulfur materials which give high values in the Copper Strip Test, while not effecting the active sulfur components which give the desired extreme pressure properties. Although this past method produced a satisfactory extreme pressure agent of a low Copper Strip corrosion, the sodium sulfide extract solution poses a serious disposal problem, since sodium sulfide is a highly offensive pollutant. An attempt was made to substitute diisobutylene for the triisobutylene to circumvent the sodium sulfide wash utilizing high pressure, e.g., 25 psig and higher, but the resultant product still required a sodium sulfide wash and the high pressure in the prior procedure tended to inactivate the sulfur to the point of detrimentally affecting the extreme pressure properties. Also sulfurized diisobutylene has the further disadvantage of crystallizing on storage whereas no crystallization problems occur with sulfurized triisobutylene.

SUMMARY OF INVENTION

We have discovered and this constitutes our invention a method of producing a sulfurized olefin having excellent extreme pressure properties of a substantially reduced Copper Strip rating, and which does not crystallize on storage or require extraction with sodium sulfide in order to produce acceptable low sensitivity to copper. Our superior and unexpected results are accomplished by a particular combination of reactants, conditions and sequential steps which result in a product of outstanding extreme pressure properties yet relatively low corrosivity towards copper and other sulfur sensitive metals. Broadly, the method of the invention comprises contacting triisobutylene with sulfur at a pressure between about 0 and 15 psig at a temperature between about 360° and 500° F. utilizing a mole ratio of triisobutylene to sulfur of between about 1:4 and 1:2.5 while blowing the reaction mixture with an inert gas at least during a portion of said contacting and recovering the sulfurized triisobutylene product of the invention from the reaction mixture.

DETAILED DESCRIPTION OF THE INVENTION

Specifically, the method comprises mixing triisobutylene with sulfur within the aforedescribed mole ratio range normally at a first temperature between about 50° and 300° F., subsequently increasing the temperature preferably to between about 375° and 465° F. for the reaction period while blowing the reaction mixture with an inert gas at least part of the time during the triisobutylene-sulfur contact, desirably at a rate of between about 0.003 and 0.2 SCFH/lb. mixture. The reaction period is normally continued until a free sulfur content of less than about 0.3 wt. % is attained. The reaction pressure is advantageously about atmospheric but pressures up to about 15 psig may be employed.

Under preferred conditions, the sulfurized triisobutylene is recovered from the reaction mixture by stripping said mixture under reduced pressure, e.g., between about 10 and 500 mm Hg. at between about 150° and 450° F. using an inert gas rate of between about 0.003 and 0.1 SCFH/lb. mixture and most preferably this is followed by a filtration of the stripped residue through standard materials such as filter paper and/or diatomaceous earth. The red colored liquid product obtained is a complex mixture of sulfur compound containing principally a 4-neopentyl-5-tertiary butyl-1,2-dithiole-3-thione and minor amounts of organic sulfides, polymeric sulfur compound, residual mercaptans and the like, essentially giving the following general analysis:

TESTS	RANGE
Sp. Gr., 60/60°F.	1.120–1.125
Kin. visc., at 100°F.	60–70
210°F.	5.5–6.0
Sulfur, wt. %	34.5–36.0
H_2S, ppm	5–40
Acetone Insolubles, wt. %	<0.01
Free Sulfur, wt. %	trace – 0.2
Aver. Mol. Wt.	260–275
Flash, COC, °F.	325–350
Copper Strip Corr. 3 hrs/250°F. a. 1 wt. % in Paraffinic Oil (125 SUS–125°F.	<4A

The inert gas employed is usually nitrogen since it is abundant and of a relatively inexpensive nature. However, other gases which are inert to the reaction are also contemplated such as carbon dioxide.

The reaction period is normally for between about 20 and 50 hours. Preferably, the reaction is periodically monitored and is judged complete when the hydrogen sulfide exit gas rate is reduced to less than about 0.6 cu. ft./hr./100 lb. charge or when no sediment (free sulfur) occurs when about 20 ccs. of sample is dissolved in about 80 ccs. of acetone. However, it is to be noted additional reaction time may be required after the aforementioned values are attained if further reduction of the copper corrosivity of the product is deemed desirable.

As heretofore stated the products of the inventive method are useful normally in amounts of between about 0.30 and 10 wt. % as extreme pressure agents in naphthenic and paraffinic lubricating oils of an SUS viscosity between about 100 and 2500 at 100° F. In addition to the subject extreme pressure product in lubricant compositions other additives may be employed such as VI improvers (e.g., polyalkylmethacrylates), detergent dispersants (e.g., alkenyl succinimides), wear inhibitors (e.g. lauryl or oleyl acid orthophosphate), rust inhibitors (e.g. oleyl amine) and lubricity agents (e.g. fatty carboxylic acids and lauryl or oleyl acid orthophosphate).

Since triisobutylene is a liquid at room temperature and of a boiling range between about 348°–354° F., the process normally does not require the use of a diluent, the excess triisobutylene functioning as such. Further, superatmospheric pressure may be employed where necessary within the limits of the parameters of the subject method in order to maintain volatile reaction ingredients in the liquid state.

One surprising feature in procedure and resultant product is pressures below about 15 psig produce a product giving a substantially lower (improved) Copper Strip rating than procedures utilizing high pressure, e.g. 25 psig or more. In the past, the art believed higher pressures resulted in a more inactive sulfur and thus a product of reduced sensitivity to copper. Another surprising feature is the importance of the maximum triisobutylene to sulfur mole ratio of greater than about 1:4 in order to obtain a low Copper Strip corrosion. Also surprising, was the fact that in the method of the invention when diisobutylene was substituted for triisobutylene a sulfurized product of substantially higher Copper Strip rating was produced.

The following examples further illustrate the invention but are not to be construed as limitations thereof.

EXAMPLE I

This example illustrates the process and product resulting therefrom of the invention.

To a 50 gallon oil heated, stirred stainless steel reactor, there was charged sulfur and triisobutylene at ambient temperature (approx. 72° F.). The resultant mixture was then heated while passing nitrogen through the product mixture at a rate of 5 SCFH. The reactor stirrer was turned on when a temperature of 300° F. was attained. Nitrogen blowing was then halted and there was then charged additional triisobutylene with triisobutylene continually taken off as overhead and recycled to the reaction. After the second triisobutylene charge the reaction was continued together with the triisobutylene recycle. The reaction mixture was then cooled coupled with reinstitution of nitrogen blowing at a rate of 10 SCFH. The pressure in the reactor was then reduced with continued nitrogen blowing to 20–25 mm Hg. absolute and the temperature was increased with continued nitrogen blowing. Nitrogen blowing was ceased and the reaction mixture was then cooled and filtered through filter paper on a 1 ft.^{2} Sparkler filter. To enhance filtration, diatomaceous earth filter aid was included.

The recovered sulfurized triisobutylene filtrate was analyzed and determined to be a complex mixture of sulfurized organic material wherein a major portion of the filtrate was identified as 4-neopentyl-5-tertiarybutyl-1,2-di-thiole-3-thione.

Several runs were made utilizing the above procedure and the reaction test data, analysis of the product and the properties of lube composition thereof are reported below in Tables I and II:

TABLE I

PROCESS DATA	RUN A		RUN B		RUN C	
Ingredient Quantities						
Sulfur, lbs.	117		117		68.4	
1st TIB, lbs.	6.8		7.0		4.1	
2nd TIB, lbs.	177.8		177.5		103.9	
N_2, SCFH	10		10		5	
Filter Aid, lbs.	1		1		1	
STEPS	Hr., F°		Hr., °F		Hr., °F.	
1. Charge S + 1st TIB	0.5	75	0.5	70	0.5	70
2. Heat + N_2 Blow	8	75–415	6	70–415	9	70–415
3. Charge 2nd TIB	51	410–417	36	410–415	25	410–415
React. + Recycle Overhead						
4. Cool + N_2 Blow	1	410–150	1	410–150	1	410–150
5. Strip (N_2 Blow), 20 mm. Hg	8	150–300	8	150–300	6	150–300
6. Cool + N_2 Blow	1	300–150	1	300–150	1	300–150
7. Filter	1	150	0.6	150	0.6	150

TABLE II

PRODUCT DATA	RUN A	RUN B	RUN C
Sulfur, wt. %	35.2	34.9	35.8
Sp. Gr., 60/60°F.	1.1233	1.1240	1.1246
Kin. Visc. at 100°F.	64.6	65.4	69.3
210°F.	5.82	5.81	5.91
Molecular Weight	262	274	270
H_2S, ppm	7	38	38
Free Sulfur, wt. %	Slight Trace	0.22	0.07
Flash, COC, °F.	354	350	330
Copper Strip Cor., 3 hr/250°F.			
*Comp. WW	3B	3B	3B
**Comp. XX	1B	1B	2A
SAE EP TEST***			
**(Comp. XX)			
1000 rpm	190	—	216
1500 rpm	182	—	166

*Comp. WW = 1 wt. % of sulfurized triisobutylene product of run + 99 wt. % paraffinic oil of 125 SUS at 100°F.

**Comp. XX = 5 wt. % sulfurized triisobutylene product of run, 92 wt. % paraffinic oil (35 wt. % of 340 SUS at 100°F. and 57 wt. % of 160 SUS at 210°F.), 1 wt. % ethyloleyl orthophosphate, 1 wt. % oleyl amine, 1 wt. % 2,5-bis (octyldithio)thiadiazole + polymer of octadecyl-butyl-, dodecyl methacrylate and tetraethylene pentamine + silicone antifoamant.

***Result in terms lb. load at failure.

EXAMPLE II

This example further illustrates the method of the invention.

To a 10 gallon reactor of the type described in Example I there were charged at ambient temperature triisobutylene and flowers of sulfur. Nitrogen blowing was instituted and continued throughout the entire reaction. The reaction mixture was heated from ambient to the desired elevated temperature and the reaction pressure adjusted via control of the nitrogen gas exit rate. At the end of the reaction period, the reaction mixture was cooled with continued nitrogen blowing, stripped under reduced pressure and filtered in a manner as heretofore described. The test data, product analysis and testing of the product in composition are set forth below in Table III and Table IV:

TABLE III

PROCESS DATA	Run D	
Ingredient Quantities		
Sulfur, lbs.	34	
TIB, lbs.	51.5	
N_2 SCFH/lb. feed	0.072	
Filter Aid, lbs.	1	
STEPS	Run D	
	Hours	°F.
1. Charge TIB+S	0.25	72
2. Pressure Reactor to 15 psig	—	72
3. React., 15 psig N_2	2.5	87–392
4. React., 15 psig N_2	10	392–430
5. React., 10 psig N_2	1	425
6. React., 0 psig N_2	21	425
7. Cool + N_2	3	320–432
8. Strip +N Blow, 20–25 mm^{2}Hg.	8	325
9. Filter	0.25	150

TABLE IV

PRODUCT DATA	Run D
Sulfur, wt. %	35.6
Sp. Gr., 60/60°F.	1.1326
Kin. vis., at 100°F.	123
210°F.	7.8
Molecular Wt.	265
H_2S, ppm	3
Free Sulfur, wt. %	Trace
Flash, COC, °F.	370
Copper Strip Cor. 3 hr/250°F. *Comp. WW	2B

*Comp. WW = 1 wt. % of sulfurized triisobutylene product of Run D + 99 wt. % paraffinic oil of 125 SUS at 100°F.

EXAMPLE III

This example illustrates the importance of starting with a substantial excess of triisobutylene.

The procedure employed, broadly, was that of Example I. Run G represents the method of the invention utilizing a 50 percent stoichiometric excess of triisobutylene and comparative Run H uses a 13 percent excess of triisobutylene.

As can be seen from the subsequent results the Copper Strip Corrosion was substantially poorer for comparative Run H than Run C.

TABLE V

PROCESS DATA	Run G	Run H
Ingredient Quantities		
Sulfur, lbs.	117.0	68.4
First TIB, lbs.	7.0	None
Second TIB, lbs.	177.5	79.2
N_2, SCFH	10	5
Filter Aid, lbs.	1	1
STEPS		
	Hr., °F.	Hr., °F.
1. Charge TIB + S	0.5 70	0.5 70
2. Heat, N_2 Blow	6 70–415	8 70–415
3. React.	36 410–415	45 410–418
4. Cool, N_2 Blow	1 410–150	1 410–150
5. Strip, N_2 Blow (25–30mm Hg.)	8 150–300	8 150–300
6. Filter	0.6 150	2 150

TABLE IV

PRODUCT DATA	Run G	Run H
Sulfur, wt. %	34.9	35.9
Sp. Gr., 60/60°F.	1.1240	1.1329
Kin. Vis., at 100°F.	65.4	66.3
210°F.	5.81	5.78
Molecular Wt.	274	264
Acetone Insol. wt. %	0.002	0.002
H_2S, ppm	38	60
Free Sulfur, wt. %	0.22	1.12
Flash, COC, °F.	350	335
Copper Strip Corr. 3 hr/250°F. *Comp. XX	1B	4B

*Same ingredients and amounts as Comp. XX in Example I except for sulfurized triisobutylene constituent substitutions.

EXAMPLE IV

This example further illustrates the criticalities of the procedural conditions particularly in respect to maintaining the pressure below about 15 psig. The procedure of Example II was essentially repeated utilizing a 50 percent excess of triisobutylene with the exception the runs employed varied pressures and the resultant sulfurized triisobutylene products were tested in the Copper Strip Corrosion Test. A synopsis of the test data and results are set forth below in Table VII:

TABLE VII

Run No.	K	L	M	N
Reaction Pressure Cycle				
25 psig, Hrs.	32	0	0	0
15 psig, Hrs.	0	0	10	0
10 psig. Hrs.	0	0	1	10
5 psig. Hrs.	0	0	0	5
0 psig, Hrs.	0	40.5	21	17
Total React. Time Hrs.	32	40.5	32	32
Reaction Temperature	410–415	410–415	425	415–430
*Copper Strip Corr. 3 hrs/250°F. Comp. YY	4C	2E	2B	2C

*Comp. YY = 6 wt. % sulfurized triisobutylene of run, 91 wt. % paraffinic oil (39 wt. % of 340 SUS at 100°F. and 52 wt. % 160 SUS at 210°F.) 1 wt. % ethyloleyl orthophosphate 1 wt. % oleyl amine, 1 wt. % 2,5-bis(octyldithio)thiadiazole + interpolymer of octadecyl-,butyl-, dodecyl methacrylate and tetraethylene pentamine + silicone antifoamant.

We claim:

1. A lubricating oil composition comprising at least about 90 wt. % hydrocarbon lubricating oil of an SUS viscosity of between about 100 and 2500 at 100° F. containing between about 0.3 and 10.0 wt. % of a sulfurized triisobutylene prepared by contacting with triisobutylene with sulfur at a temperature between about 360° and 500° F. under a pressure of between about 0 and 15 psig utilizing a mole ratio of triisobutylene to sulfur of between 1:4 and 1:2.5 while blowing the reaction mixture with an inert gas during at least a portion of said contacting and continuing the reaction until the free sulfur in the final reaction mixture is less than about 0.3 wt. % and recovering the sulfurized triisobutylene from the reaction mixture.

2. A composition in accordance with claim 1 wherein said recovering comprises stripping the reaction mixture at a temperature between about 150° and 450° F., under a pressure between about 10 and 500 mm Hg. with blowing of inert gas therethrough and subsequently filtering the residue to recover said product as filtrate.

3. A composition in accordance with claim 2 wherein said inert gas is nitrogen.

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