United States Patent Office 3,644,433 Patented Feb. 22, 1972

3,644,433

INCREASING AUTOIGNITION TEMPERATURE OF CS_2

John A. Bichard, Point Edward, Ontario, and Jackson Eng, Sarnia, Ontario, Canada, assignors to Esso Research and Engineering Company

No Drawing. Filed Mar. 20, 1970, Ser. No. 21,489
Int. Cl. C23g 5/04
U.S. Cl. 252—364 2 Claims

ABSTRACT OF THE DISCLOSURE

A composition of matter suitable for cleaning oil and gas wells and for sulfiding a hydrotreating catalyst which comprises carbon disulfide containing 5–40 lv. percent, preferably 10–30%, of a refinery stream boiling below 250° F., chosen from the group consisting of catalytically cracked naphtha and coker naphtha.

BACKGROUND OF THE INVENTION

This invention relates to a carbon disulfide composition having increased autoignition temperature.

In the petroleum industry, carbon disulfide is used for sulfiding hydrotreating catalysts, or as a solvent for dewaxing and sulfur removal at the wellbores of oil and gas wells to increase flow. Because of its low autoignition temperature of 240° F. carbon disulfide is hazardous and there is reluctance to store and handle this material. Thus a cheap, relatively available agent which would raise its autoignition temperature would permit more effective and safer use of carbon disulfide.

It has already been shown in U.S. Pat. 3,375,192, issued Mar. 26, 1968 to Rowlinson of Canadian Industries Ltd., that the autoignition temperature of CS_2 can be increased by the addition of 8 to 16% by volume of n-pentane. Petroleum naphtha and chlorinated hydrocarbons are shown to be substantially less effective in increasing the autoignition temperature of CS_2. These data on n-pentane have been confirmed and extended to other paraffins and naphthenes. However such compounds are expensive. On the other hand refinery streams would be cheap and easily available.

SUMMARY OF THE INVENTION

It has now been surprisingly discovered that 5 to 40 liquid volume percent of catalytically cracked and coker naphthas boiling below 250° F. when added to carbon disulfide results in a large increase in the autoignition temperature of the carbon disulfide.

Thus the novel composition of this invention comprises a mixture of carbon disulfide and 5 to 40 lv. percent (preferably 10–30%) of a refinery stream boiling below 250° F., chosen from the group consisting of catalytically cracked naphtha and coker naphtha.

The carbon disulfide naphtha mixtures of the above type have an ignition temperature between 490° F. for 10 lv. percent of catalytically cracked naphtha boiling 170–250° F. and 700° F. for 30 lv. percent of catalytically cracked naphtha. The comparable autoignition temperature range for coker naphtha boiling 160–190° F. lies between 495° F. and 660° F. For comparison, autoignition temperature of carbon disulfide alone is 240° F.

These compositions possess satisfactory solvent power for waxes and sulfur found in oil and gas wells and are also suitable for sulfiding catalysts.

When used as well solvent the novel composition of this invention is pumped down the well and allowed to remain until the wax and sulfur has been dissolved after which it is removed from the well.

When used to presulfide a hydrotreating catalyst the composition is passed over the catalyst, generally, in the presence of hydorgen at a temperature in the neighborhood of the subsequent reaction temperature until the catalyst is fully sulfided, after which the flow of composition is stopped.

DETAILED DESCRIPTION

A synergistic effect occurs when the autoignition temperature of admixtures of an added component with carbon disulfide is higher than either the carbon disulfide or added component alone. The present studies confirm that n-pentane at concentrations of 10 and 30 liquid volume percent (lv. percent) increases the autoignition temperature of CS_2. Several other normal and isoparaffins and naphthenes also resulted in a synergistic autoignition effect. However, an aromatic, such as benzene, added at 10 and 30 lv. percent concentration, did not raise the autoignition temperature. Toluene and xylene were only slightly more effective than benzene.

The following example shows that catalytically cracked and coker naphthas boiling below 250° F. gave the largest increase in autoignition temperature of carbon disulfide. This is unexpected since these light cracked naphthas contain aromatics. A comparison with other compounds including check runs on n-pentane and straight-run petroleum naphtha is included. The flammability studies were made in accordance with ASTM procedure D–287–55.

EXAMPLE 1

A series of solutions was made consisting of carbon disulfide in admixture with various hydrocarbons and refinery streams having the following inspections.

INSPECTIONS ON REFINERY STREAMS USED IN AUTOIGNITION STUDIES

Type	Naphtha					Gas oil				
	Virgin (rainbow)	Udex raffinate	Cat cracked	Steam cracked	Coker	Turbo Fuel	St. run light	Cat cracked	Steam cracked	Coker
Gravity, ° API	74.5	73.2	57.5	29.8	64.5	47.2	32.2	22.0	13.4	33.2
Distillation, ASTM ° F.:										
IBP	108	136	108	204	92	285	516	394	376	320
5%	127	148	128	216	124	309	544	438	418	381
10%	130	152	136	221	134	317	560	454	423	413
20%	137	156	149	238	148	327	572	474	431	467
30%	141	160	164	247	159	335	580	488	437	505
40%	146	164	185	258	168	343	586	501	442	534
50%	152	169	208	272	177	351	592	517	446	556
60%	157	175	234	290	186	360	597	534	452	574
70%	163	184	260	309	196	370	606	550	460	594
80%	170	197	293	333	209	384	616	572	473	613
90%	180	222	323	355	227	401	632	601	490	645
95%	188	260	344	370	239	415	650	629	509	674
FBP	229	320	390	385	287	456	654	640	549	678
Bromine Number	<0.1	4.5	99.2	69.5	150.2	0.5	5.0	19.4	37.8	25.6
FIA, lv. percent:										
Saturates	95	90	22	7	19	82	61	26	8	
Olefins	0	0	24	93	73	0	0	9	92	
Aromatics	5	10	24		8	18	39	65		
Isopentane LV percent	4	1	[1] 5.7	0	[2] 0.3	0	0	0	0	0
n-Pentane LV percent	8	4.5	[1] 0.6	0.1	[2] 1.4	0	0	0	0	0
Total pentanes, LV percent	12	5.5	6.3	0.1	1.7	0	0	0	0	0

([1])i-170° F.—Pentanes LV percent—19.0. 170–250° F.—Pentanes LV percent —0.0.
([2])i-160° F.—Pentanes LV percent 5.1. 160–190° F.—Pentanes LV percent—0.0.

The following data were obtained.

AUTOIGNITION TEMPERATURE OF CARBON DISULPHIDE AND HYDROCARBON MIXTURES

	Hydrocarbon added to CS_2, LV percent			
	0	10	30	100
	Autoignition temperature, ° F.			
Pure hydrocarbons:				
n-Pentane	240	515	720	485
i-Pentane	240	525	725	650
Pentene-1	240	485	650	530
n-Hexane	240	400	640	430
Methylcyclopentane	240	455	615	495
Cyclohexane	240	405	580	495
Benzene	240	220	225	1,040
Toluene	240	255	365	955
Xylene	240	265	375	955
Refinery streams:				
Naphthas:				
Virgin	240	415	645	475
Raffinate	240	395	510	460
Catalyst cracked	240	490	700	505
Catalyst cracked fraction:				
i-170	240	540	700	535
170–250	240	490	665	510
250–390	240	375	440	565
Steam cracked	240	390	435	805
Coker	240	505	680	485
Coker fraction:				
i-160	240	500	660	505
160–190	240	495	660	490
190–287	240	430	565	480
Gas oils:				
Jet fuel	240	370	380	455
Straight run light	240	235	360	440
Light catalyst cracked	240	350	350	660
Steam cracked	240	370	355	800
Coker	240	340	370	455

The above data clearly show that besides normal pentane, other pure hydrocarbon, e.g. isopentane, pentene-1, normal hexane, methylcyclopentane and cyclohexane all increase the autoignition temperature of carbon disulfide. At 30 lv. percent they all have a higher value than either CS_2 or the additive alone.

What is more important and more surprising is the fact that catalytically cracked naphtha and coker naphthas boiling below 250° F. increase the autoignition temperature of CS_2 despite their aromatic content. A synergistic effect is noted at 30 lv. percent. This effect is not due to the presence of pentane since the amount of pentane in the CS_2 containing 30 lv. percent catalytically cracked naphtha, for example, was 2.1%. At this pentane concentration, the autoignition temperature of CS_2 is only raised to 250° F., while the CS_2–30 lv. percent mixture of catalytically cracked naphtha had an autoignition temperature of 700° F. indicating that other components of the naphtha have a very beneficial and unexpected effect in raising the autoignition temperature of CS_2.

No important increase is noted with benzene and only a small increase with toluene and xylene. Virgin naphtha and raffinate from Udex extraction and steam cracked naphtha, or any of the gas oils show significantly smaller increase in autoignition temperature than catalytically cracked and coker naphtha boiling below 250° F.

The nature and advantages of the present invention having thus been fully set forth and specific examples of the same given, what is claimed as new, useful and unobvious is:

1. A composition of matter consisting essentially of carbon disulfied containing 5–40 liquid volume percent of a refinery stream boiling below 250° F. selected from the group consisting of catalytically cracked naphtha and coker naphtha.

2. The composition of claim **1** in which the carbon disulfide contains 10–30 liquid volume percent of the refinery stream.

References Cited

UNITED STATES PATENTS

3,279,541	10/1966	Knox et al.	252—8.55 X
3,375,192	3/1968	Rowlinson	252—8.55 X
3,437,146	4/1969	Everhart et al.	166—304 X
3,558,509	1/1971	Wiewiorowski et al.	252—364

HERBERT B. GUINN, Primary Examiner

U.S. Cl. X.R.

23—206; 166—304, 312; 252—8.55 B, 439