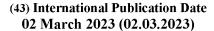
#### (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau





English



(10) International Publication Number WO 2023/027699 A1

(51) International Patent Classification:

 C10M 135/10 (2006.01)
 C10N 40/02 (2006.01)

 C10N 20/02 (2006.01)
 C10N 40/04 (2006.01)

 C10N 30/02 (2006.01)
 C10N 40/12 (2006.01)

(21) International Application Number:

PCT/US2021/047444

(22) International Filing Date:

25 August 2021 (25.08.2021)

(25) Filing Language:

(26) Publication Language: English

- (71) Applicant: EXXONMOBIL TECHNOLOGY AND ENGINEERING COMPANY [US/US]; 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).
- (72) Inventor: WANG, Lin; 2800 Mountain Laurel Drive, Furlong, PA 18925 (US).
- (74) Agent: KAISEER, Iona et al.; VORYS, SATER, SEY-MOUR AND PEASE LLP, 909 Fannin Street, suite 2700, Houston, Texas 77010 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

#### Published:

— with international search report (Art. 21(3))



(57) **Abstract:** Compositions and corresponding methods are provided for using a narrow compositional range of calcium alkylnaphthalene sulfonate in industrial oils, such as lubricant oils, to provide unexpected demulsification properties to the industrial oils. The calcium alkylnaphthalene sulfonate can be present in an industrial oil composition in an amount between 0.30 wt% and 0.75 wt% of the composition.

### INDUSTRIAL OIL WITH LOW TEMPERATURE DEMULSIBILITY

#### **FIELD**

[0001] Compositions are provided related to high viscosity circulating oils with improved properties for low temperature demulsibility.

### **BACKGROUND**

[0002] Circulating oils refer to a type of lubricant that is typically used in a variety of applications such as lubrication of bearings, gears / gearboxes, blowers, pumps, turbines, and/or other types of equipment. A circulating oil system can provide a continuous flow of lubricant to target surfaces for lubrication. In many situations, the circulating oil can be exposed to adverse environmental conditions which allow introduction of contaminants into the lubricant, which can include water and/or various types of particulate contamination.

[0003] One desirable feature of a circulating oil can be demulsibility. As a circulating oil becomes exposed to water, the water can be incorporated into the oil as an emulsion. If the water remains as an emulsion in the oil, the amount of water in the emulsion can accumulate over time, leading to reduced effectiveness for the lubricant. Demulsibility refers to the ability of an oil composition to undergo phase separation in a relatively short period of time to form separate oil and water phases. This can reduce or minimize the amount of emulsified water present in the oil, thus allowing the oil to maintain target lubricating properties for an increased period of time.

[0004] U.S. Patent 3,764,533 describes oil soluble dialkaryl sulfonate compositions. The metal ion for the sulfonate compositions is described as being any convenient neutralizing metal, including ammonia or amines. Examples of use of the composition in lubricating oils show use of 0.10 wt% or 0.12 wt% of a barium salt.

### **SUMMARY**

[0005] In an aspect, an industrial oil or lubricating oil composition is provided. The composition includes 0.30 wt% to 0.75 wt% of one or more calcium alkylnaphthalene sulfonates. Additionally, the composition includes one or more base oils. Optionally, the oil composition can have a kinematic viscosity at 40°C of 130 cSt to 1000 cSt. Optionally, the oil composition can include 0.30 wt% to 0.48 wt% of the one or more calcium alkylnaphthalene sulfonates. Optionally, the oil composition can include 0.52 wt% to 0.75 wt% of the one or more calcium alkylnaphthalene sulfonates.

[0006] In some aspects, each calcium alkylnaphthalene sulfonate can include one or more alkyl side chains, the one or more alkyl side chains having a total length of 8 to 24 carbons. For example, the one or more calcium alkylnaphthalene sulfonates can correspond to one or more

calcium dialkylnaphthalene sulfonates. Optionally, the one or more calcium dialkylnaphthalene sulfonate can include alkyl side chains having a length of 4 to 12 carbons. Optionally, the one or more calcium alkylnaphthalene sulfonates can include calcium dinonylnaphthalene sulfonate.

[0007] Optionally, the one or more base oils can correspond to a Group I base oil, a Group II base oil, a polyalphaolefin base oil, or a combination thereof. Optionally, the oil composition have a viscosity index of 50 or more and/or a viscosity index of 200 or less.

[0008] In some aspects, the oil composition can have a demulsification time according to ASTM D1401 at 54°C that is less than or equal to a demulsification time according to ASTM D1401 at 82°C.

[0009] In some aspects, the oil composition can be used as a circulating oil, lubricant, or a combination thereof for a system comprising a circulating oil system, a turbine, a gear box, a blower, a pump, or a combination thereof. Optionally, the oil composition can be used at a temperature of -20°C to 100°C, or -20°C to 55°C.

## **DETAILED DESCRIPTION**

[0010] All numerical values within the detailed description and the claims herein are modified by "about" or "approximately" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

# Overview

[0011] In various aspects, compositions and corresponding methods are provided for using a narrow compositional range of calcium alkylnaphthalene sulfonate in industrial oils (such as lubricant oils) to provide unexpected demulsification properties to the industrial oils. The calcium alkylnaphthalene sulfonate can be present in an industrial oil composition in an amount between 0.30 wt% and 0.75 wt% (or 0.30 wt% to 0.48 wt%) of the composition.

[0012] Alkylnaphthalene sulfonates are traditionally used as rust inhibitors for industrial oil compositions, although they are known to also have some demulsification benefits. It is well understood that conventional additives for demulsifying an industrial oil / lubricant oil should result in a composition where demulsification occurs more rapidly at higher temperatures. However, it has been unexpectedly discovered that, for compositions having a suitable range of kinematic viscosities, use of calcium alkylnaphthalene sulfonate can provide an equivalent and/or faster rate of demulsification at lower temperatures (such as 54°C) when compared with the rate of demulsification at higher temperatures (such as 82°C). The unexpected feature of equivalent and/or faster rate of demulsification at lower temperatures is not observed when metal ions different from calcium are used as part of an alkylnaphthalene sulfonate salt. Similarly, the

-3-

unexpected demulsification rate feature at lower temperatures is not observed when counter-ions different from sulfonate are used.

In various aspects, an oil composition can include one or more types of calcium alkylnaphthalene sulfonate, with the total weight of calcium alkylnaphthalene sulfonates in the composition corresponding to 0.30 wt% to 0.75 wt% (or 0.30 wt% to 0.48 wt%) of the composition. Suitable calcium alkylnaphthalene sulfonates can include one or more side alkyl side chains attached to the naphthalene, such as two or more side chains. The total number of carbons in the one or more side chains (i.e., not including carbons in the naphthalene rings) can correspond to 8 to 24 carbon atoms, or 12 to 24 carbon atoms. When two or more side chains are present, each side chain can include at least 4 carbon atoms, or at least 6 carbon atoms, such as 4 to 12 carbon atoms, or 6 to 12 carbon atoms. Optionally, a calcium alkylnaphthalene sulfonate can be a calcium dialkylnaphthalene sulfonate, so that there are two alkyl side chains attached to the naphthalene. Calcium dinonylnaphthalene sulfonate is an example of such a composition.

[0014] In this discussion, the term "alkyl" is defined to include straight-chain or branched alkyl groups. For example, a butyl group can correspond to n-butyl (straight-chain), i-butyl (branched, butyl group bonded to naphthalene via a carbon that also has two bonds to hydrogen atoms), or t-butyl (branched, butyl group bonded to naphthalene via a carbon that has no bonds to hydrogen atoms).

In various aspects, the amount of the calcium alkylnaphthalene sulfonate in the lubricating oil composition can correspond to 0.30 wt% to 0.75 wt% of the composition, or 0.30 wt% to 0.60 wt%, or 0.30 wt% to 0.48 wt%, or 0.30 wt% to 0.45 wt%, or 0.35 wt% to 0.60 wt%, or 0.35 wt% to 0.48 wt%, or 0.35 wt% to 0.45 wt%, or 0.52 wt% to .75 wt%. This amount can correspond to a single type of calcium alkylnaphthalene sulfonate (such as calcium dinonylnaphthalene sulfonate), or this amount can correspond to a mixture of calcium alkylnaphthalene sulfonates. It is noted that the unexpected feature of faster demulsification at lower temperatures can be achieved for amounts of calcium alkylnaphthalene sulfonate that are greater than 0.75 wt%, but higher concentrations result in still slower demulsification times at higher temperatures, which may be less desirable in some applications.

[0016] In various aspects, one or more calcium alkylnaphthalene sulfonates can be used as an additive for an industrial oil / lubricating oil composition. The oil composition can also optionally include one or more other additives, such as any convenient type of additive typically found in a lubricating oil composition. Examples of additives include (but are not limited to)

-4-

antioxidants, metal deactivators, pour point depressants, and anti-foaming agents. In some aspects, the lubricating oil composition can correspond to a Group I lubricant, a Group II lubricant, a polyalphaolefin, or a combination thereof. In some aspects, the lubricating oil composition can include 80 wt% to 99.5 wt% of a Group I base oil, a Group II base oil, or a combination thereof. In some aspects, the lubricating oil composition can have a viscosity index of 50 or more, or 70 or more, or 80 or more, or 85 or more, such as up to 200 or possibly still higher. In some aspects, the viscosity index can be 70 to 170, or 70 to 130, or 80 to 170, or 80 to 130. In some aspects, the lubricating oil composition can have a kinematic viscosity at 40°C (also referred to as KV40) of 130 cSt or more, or 150 cSt or more, or 200 cSt or more, or 320 cSt or more, or 360 cSt or more, or 400 cSt or more, such as up to 1000 cSt or possibly still higher.

[0017] In some aspects, the industrial oil / lubricating oil composition including 0.30 wt% to 0.75 wt% of calcium alkylnaphthalene sulfonate (or 0.30 wt% to 0.48 wt%) can be used as a lubricant in a circulating oil system. Additionally or alternately, the lubricating oil composition can be used as a lubricant for a turbine, a gear box, a blower, a pump, or a combination thereof. Further additionally or alternately, the lubricating oil composition can be used as a lubricant for bearings, gears, or a combination thereof. The lubricating oil composition can be used as a lubricant at a temperature between -20°C and 100°C, or -20°C and 70°C, or -20°C to 55°C, or 0°C to 100°C, or 0°C to 55°C.

### Additional Additives for Oil Compositions

[0018] An industrial oil / lubricating oil composition can optionally include one or more additives. Such additives can include, but are not limited to, antiwear additives, detergents, dispersants, viscosity modifiers, corrosion inhibitors, rust inhibitors, metal deactivators, extreme pressure additives, anti-seizure agents, wax modifiers, other viscosity modifiers, fluid-loss additives, seal compatibility agents, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see "Lubricant Additives, Chemistry and Applications", Ed. L. R. Rudnick, Marcel Dekker, Inc. 270 Madison Ave. New York, N.J. 10016, 2003, and Klamann in Lubricants and Related Products, Verlag Chemie, Deerfield Beach, FL; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, NJ (1973); see also U.S. Patent No. 7,704,930, the disclosure of which is incorporated herein in its entirety. These additives are commonly delivered with varying amounts of diluent oil that may range from 5 weight percent to 50 weight percent.

-5-

[0019] The additives useful in this disclosure do not have to be soluble in the lubricating oils. For example, insoluble additives such as zinc stearate in oil can be dispersed in the lubricating oils of this disclosure.

[0020] When lubricating oil compositions contain one or more additives, the additive(s) are blended into the composition in an amount sufficient for it to perform its intended function. Additives are typically present in lubricating oil compositions as a minor component, typically in an amount of less than 50 weight percent, preferably less than 30 weight percent, and more preferably less than 15 weight percent, based on the total weight of the composition. Additives are most often added to lubricating oil compositions in an amount of at least 0.1 weight percent, preferably at least 1 weight percent, more preferably at least 5 weight percent. Typical amounts of such additives useful in the present disclosure are shown in Table 1 below.

[0021] It is noted that many of the additives are shipped from the additive manufacturer as a concentrate, containing one or more additives together, with a certain amount of base oil diluents. Accordingly, the weight amounts in the Table 1 below, as well as other amounts mentioned herein, are directed to the amount of active ingredient (that is the non-diluent portion of the ingredient). The weight percent (wt%) indicated below is based on the total weight of the lubricating oil composition.

TABLE 1

Typical Amounts of Other Lubricating Oil Components

	Approximate	Approximate
Compound	wt% (Useful)	wt% (Preferred)
Dispersant	0.1-20	0.1-8
Detergent	0.1-20	0.1-8
Friction Modifier	0.01-5	0.01-1.5
Antioxidant	0.1-5	0.1-1.5
Pour Point Depressant (PPD)	0.0-5	0.01-1.5
Anti-foam Agent	0.001-3	0.001-0.15
Viscosity Modifier (solid polymer basis)	0.1-2	0.1-1
Antiwear	0.2-3	0.5-1
Inhibitor and Antirust	0.01-5	0.01-1.5

[0022] The foregoing additives are all commercially available materials. These additives may be added independently but are usually precombined in packages which can be obtained from suppliers of lubricant oil additives. Additive packages with a variety of ingredients, proportions and characteristics are available and selection of the appropriate package will take the requisite use of the ultimate composition into account.

# **Examples**

[0023] In this discussion, including the examples, the following methods were used to characterize lubricant base oils. Demulsibility at 54°C or 82°C was determined according to ASTM D1401. Kinematic viscosity at 40°C (KV40) was determined according to ASTM D445. Rust inhibition was determined according to ASTM D665, procedure A. Copper strip corrosion testing was determined according to ASTM D130, either procedure 1B or 1A as specified below.

[0024] In the examples that follow, calcium dinonylnaphthalene sulfonate was used as the calcium alkylnaphthalene sulfonate. The calcium dinonylnaphthalene sulfonate was introduced into the lubricant oil compositions by adding NA-SUL® 729, a rust inhibitor that is commercially available from King Industries of Norwalk, CT. It is noted that this commercially available product includes roughly 50 wt% calcium dinonylnaphthalene sulfonate in a light mineral oil. Thus, the content of calcium dinonylnaphthalene sulfonate in the Examples below is roughly half of the content of the NA-SUL® 729.

### Example 1 – Demulsibility Performance for Group I Base Oil

[0025] A series of lubricating oil compositions were formed using a Group I base oil correspond to a mixture of Americas CORE™ 2500 and Americas CORE™ 600, both commercially available from ExxonMobil Corporation. In the first composition (Composition A1), NA-SUL® 729 (containing 50 wt% of calcium dinonylnaphthalene sulfonate) was added as a rust inhibitor and a demulsifier. An additive including an antioxidant and a metal deactivator (Additive #1) was also added, along with additives corresponding to a pour point depressant (PPD) and an anti-foaming agent (AF). As will be demonstrated in Example 2, these additional additives are not responsible for the unexpected demulsification performance observed in Composition A1. For comparison, similar lubricant oil compositions (Compositions C1 − C4) were formed based on Americas CORE™ 2500 and Americas CORE™ 600, but with a different commercially available rust inhibitor additive (Lubrizol® 5158). For some of these additional lubricant oil compositions (C2 − C4), other commercially available polyethylene glycol-based demulsifiers were also added (Pluronic L 121, Tolad® 9312, Lubrizol® 5957). Table 1 shows the compositions and

-7-

corresponding characterization results. As noted above, the 0.75 wt% value of NA-SUL® 729 in Table 1 corresponds to 0.375 wt% of calcium dinonylnaphthalene sulfonate.

Table 1 - Demulsibility for Group I Lubricant Oil Compositions

	A1	C1	C2	C3	C4
Americas CORE 2500	95.71	96.81	96.79	96.78	96.78
Americas CORE 600	2.84	2.84	2.84	2.84	2.84
NA-SUL 729	0.75				
Additive #1	0.17				
Lubrizol 5158		0.3	0.3	0.3	0.3
Pluronic L 121			0.02		
Tolad 9312				0.03	
Lubrizol 5957					0.03
Others(such as AF or PPD)	0.53	0.05	0.05	0.05	0.05
Total	100	100	100	100	100
ASTM D445-kinematic	460 <sup>[1]</sup>	444.1	443.6	442.8	441.9
viscosity at 40°C (cSt)					
ASTM D1401 @ 54C, time	10	>60(47ml	60	35	50
to 3 ml emulsion, min		of emulsion			
		at the end of			
		60-min test)			
ASTM D1401 @ 82C, time	10	20	5	5	5
to 3 ml emulsion, min					
ASTM D665, procedure A	Pass	Pass	uni	-	
ASTM D130, what	1B	1A	20	2.	
procedure?					

[0026] As shown in Table 1, the demulsification rate determined according to ASTM D1401 for Composition A1 was 10 minutes at both 54°C and 82°C. This is in contrast to (comparative) Compositions C1 – C4, where the demulsification at 54°C required 35 minutes or greater while demulsification occurred in 20 minutes or less at 82°C. Thus, addition of calcium alkylnaphthalene sulfonate to the composition corresponding to Sample A1 resulted in unexpectedly fast demulsification at 54°C, with the further unexpected result of the demulsification at 54°C occurring at the same rate as demulsification at 82°C.

# Example 2 – Comparison of Sulfonate Compositions

[0027] Additional compositions were made to investigate how changing various features of a sulfonate compound would impact the demulsification behavior. Table 2 shows results from testing of these additional compositions. Compositions A2 and A3 are additional inventive compositions that show a range of concentrations where calcium dinonylnaphthalene sulfonate can cause a composition to demulsify at lower temperature (54°C) at the same or a faster rate than a higher temperature (82°C). As noted above, the concentration of calcium dinonylnaphthalene sulfonate in NA-SUL® 729 is roughly 50 wt%, so Composition A2 corresponds to a calcium

dinonylnaphthalene sulfonate concentration of 0.375 wt%, while Composition A3 corresponds to a concentration of 0.75 wt%. Composition C5 is a comparative example that uses zinc dinonylnaphthalene sulfonate. The amount of zinc dinonylnaphthalene sulfonate in NA-SUL® ZS is roughly 42 wt%, so the concentration of zinc dinonylnaphthalene sulfonate in Composition C5 is ~0.32 wt%. Composition C6 is a comparative example that uses barium dinonylnaphthalene sulfonate. The amount of barium dinonylnaphthalene sulfonate in NA-SUL® BSN is roughly 51 wt%, so the concentration of barium dinonylnaphthalene sulfonate in C6 is ~0.38 wt%. Composition C7 is a comparative example that uses HiTEC® 614, a neutral sulfonate detergent that includes calcium nonylbenzene sulfonate (i.e., a single aromatic ring, and only one nonyl side chain).

Table 2 – Comparison of Sulfonate Compounds

	A2	A3	C5	C6	C7
Americas Core 2500	96.41	95.66	96.41	96.41	96.41
Americas Core 600	2.84	2.84	2.84	2.84	2.84
NA-SUL 729	0.75	1.50			
NA-SUL ZS			0.75		
NA-SUL BSN				0.75	
HiTEC 614					0.75
Total	100	100	100	100	100
ASTM D1401@ 54°C, time to 3 ml emulsion, min	15	5	>30	>30	>30
ASTM D1401@ 82°C, time to 3 ml emulsion, min	15	25	30	15	>60

[0028] It is noted that for Compositions C5, C6, and C7, the demulsification time according to ASTM D1401 at 54°C is shown as greater than 30 minutes. This means that substantially more than 3 ml of emulsion remained after 30 minutes. Therefore, the demulsification time according to ASTM D1401 at 54°C for Compositions C5 and C6 is slower than at 82°C by definition, as the ASTM D1401 demulsification test at 82°C completed within 30 minutes for Compositions C5 and C6. For Composition C7, the demulsification test failed to complete at both 54°C and at 82°C, indicating a composition with undesirable demulsification properties.

[0029] It is further noted that for all of the compositions in Table 2, the only additive that was added to the base oil mixture is the demulsifier. This demonstrates that the unexpected demulsifying behavior is due to the demulsifier, and not some other additive.

# Example 3 - Demulsibility Performance for Group I Oil versus Group II Oil

[0030] Additional compositions were made to compare demulsifying performance in lubricant base oil compositions based on Group I base oils versus Group II base oils. Table 3 shows

this comparison. In Table 3, Composition B1 corresponds to a lubricant oil composition based on a Group II base oil. The major component in the Group II base oil corresponded to a base oil X with a kinematic viscosity at 40°C between 460 cSt and 520 cSt, a viscosity index between 95 and 115, and a clear and bright appearance. Some EHC 45 base oil (available from ExxonMobil Corporation) was also included in the composition. Additionally, the additive mixture corresponding to "Additive #1" from Table 1 was included, as well as various amounts of additional anti-foaming agents and pour point depressants. Table 3 also shows Composition A1 from Table 1, as well as two additional Compositions (A4 and A5) corresponding to Group I lubricant oil compositions.

Table 3 - Comparison of Demulsification for Group I and Group II Oils

	B1	A1	A4	A5
"Base oil X" (Group II)	96.45			
EHC 45	2.5			
Americas Core 2500		95.71	96,11	95.91
Americas Core 600		2.84	2.84	2.84
NA-SUL 729	0.75	0.75	0.75	0.75
Additive #1	0.17	0.17	0.17	0.17
Others(such as AF or PPD)	0.13	0.53	0.13	0.33
Total	100	100	100	100
ASTM D445-kinematic viscosity at 40°C (cSt)	454.7	460 (estimate)	460 (estimate)	460 (estimate)
ASTM D1401 @ 54°C, time to 3 ml emulsion, min	10	10	10	10
ASTM D1401 @ 82°C, time to 3 ml emulsion, min	30	10	20	35
ASTM D665, procedure A	Pass	Pass	Pass	Pass
ASTM D130, what procedure?	1B	1B	1A	1A

[0031] As shown in Table 3, addition of calcium dinonylnaphthalene sulfonate also provided unexpected demulsifying behavior for the Group II lubricant oil composition corresponding to Composition B1. Based on Table 3, it is believed that calcium alkylnaphthalene sulfonate is generally effective, when used at a suitable concentration, for providing unexpected demulsifying behavior for lubricant oil compositions with viscosity indexes between 50 - 200, or 70 - 130, or 80 - 120.

# Example 4 – Variations in Rust Inhibitor for Group II Lubricant Oils

[0032] The alternative rust inhibitors and polyethylene glycol-based demulsifiers from Example 1 were also tested in Group II lubricant oils. Table 4 shows the results from testing of various compositions containing Group II base oils. It is noted that NA-SUL® CA-1089 is a mixed sulfonate and carboxylate composition. Although the concentration of NA-SUL® CA-1089 is

- 10 -

lower, the concentration is representative of the amount that would typically be used for rust inhibition. HiTEC® 536 is a succinimide rust inhibitor. Lubrizol 5158 is also a rust inhibitor. Tolad 9312 is a glycol-based demulsifier. It is noted that the first column in Table 4 is the same as the first column in Table 3.

Table 4 - Rust Inhibitors for Group II Lubricant Oils

	B1	C8	C9	C10
Midas #	20-57571	20-53669	20-55208	20-43142
"Base oil X" (Group II)	96.45	97.17	97.34	97.17
EHC 45	2.5	2.5	2.5	2.5
NA-SUL 729	0.75			
NA-SUL CA-1089		0.1		
HiTEC 536			0.1	
Lubrizol 5158				0.3
Additive #1	0.17	0.17		
Tolad 9312		0.03	0.03	
Others( such as AF or PPD)	0.13	0.13	0.03	0.03
Total	100	100	100	100
ASTM D445-kinetic viscosity at	454.7	455.3	æ	457.7
40°C (cSt)				
ASTM D1401 @ 54°C, time to 3 ml	10	>30(45ml	>30(56 ml	>60(12 ml
emulsion, min		emulsion at	emulsion at	emulsion at
		the end of 30-	the end of 30-	the end of the
		min test)	min test)	test)
ASTM D1401 @ 82°C, time to 3 ml	30	10	30	20
emulsion, min				
ASTM D665, procedure A	Pass	Pass	Pass	20
ASTM D130, what procedure?	1B	1A	1B	~

[0033] As shown in Table 4, the other additives tested in Compositions C8, C9, and C10 do not provide the unexpected demulsifying benefit of calcium alkylnaphthalene sulfonate.

# Example 5 – Variations in Additive Concentration

[0034] Additional compositions were made to determine the range of calcium alkylnaphthalene sulfonate that can be effective for producing the unexpected demulsifying behavior. Table 3 shows compositions that contain varying amounts of calcium dinonylnaphthalene sulfonate. (As mentioned above, roughly 50 wt% of NA-SUL® 729 corresponds to calcium dinonylnaphthalene sulfonate.)

Table 5 - Variations in Additive Concentration

	B1	C11	B2	B3
"Base oil X" (Group II)	96.45	97.0	95.7	96.35
EHC 45	2.5	2.5	2.5	2.5
Na-Sul 729	0.75	0.5	1.5	0.75
Na-sul Ca-1089				
Additive #1	0.17		0.17	0.17

PX-3843				0.1
Others( such as AF or PPD)	0.13		0.13	0.13
Total	100	100	100	100
ASTM D445-kinematic viscosity at	454.7	463.4	455,5	
40°C (cSt)				
ASTM D1401 @ 54°C, time to 3 ml	10	>30 (67ml	5	10
emulsion, min ( shorter is better)		emulsion at		
		the end of 30-		
		min test		
		period)		
ASTM D1401 @ 82°C, time to 3 ml	30	>60(48 ml	>60( 7ml	45
emulsion, min		emulsion at	emulsion at	
		the end of 60-	the end of 60-	
		min test	min test)	
		period)		
ASTM D665, procedure A	Pass	Fail	Pass	-
ASTM D130, what procedure?	1B	1B	<b></b>	J.

[0035] In Table 5, the first column corresponds to the composition from the first column in Table 3. The second column (Composition C11) is a comparative example, where the concentration of calcium dinonylnaphthalene sulfonate is only 0.25, and therefore is too low to provide the unexpected benefit. The third column (Composition B2) is a composition that is at the upper limit for the calcium alkylnaphthalene sulfonate concentration. It is noted that for the D1401 test at 82°C, only 7 ml of water remained in emulsion at the end of the time period, showing the substantial demulsification was still occurring, although on a slower time scale. Thus, Composition B2 could potentially be suitable for use as a lubricating oil in some lubricating environments. Composition B3 differs from Composition B1 only due to the presence of additional additive PX-3843, which is an additional demulsifier that contains a combination of tricresyl phosphate and an ethylene oxide / propylene oxide co-polymer. As shown in Table 5, this additional demulsifier does not modify the unexpected demulsifying behavior achieved by including a calcium alkylnaphthalene sulfonate in composition B3.

### Additional Embodiments

[0036] Embodiment 1. An industrial oil or lubricating oil composition, comprising: 0.30 wt% to 0.75 wt% of one or more calcium alkylnaphthalene sulfonates; and one or more base oils, the oil composition comprising a kinematic viscosity at 40°C of 130 cSt to 1000 cSt.

[0037] Embodiment 2. The oil composition of Embodiment 1, wherein the oil composition comprises 0.30 wt% to 0.48 wt% of the one or more calcium alkylnaphthalene sulfonates.

- [0038] Embodiment 3. The oil composition of any of the above embodiments, wherein each calcium alkylnaphthalene sulfonate comprises one or more alkyl side chains, the one or more alkyl side chains comprising a total length of 8 to 24 carbons.
- [0039] Embodiment 4. The oil composition of any of the above embodiments, wherein the one or more calcium alkylnaphthalene sulfonates comprise one or more calcium dialkylnaphthalene sulfonates.
- [0040] Embodiment 5. The oil composition of Embodiment 4, wherein the one or more calcium dialkylnaphthalene sulfonate comprise alkyl side chains having a length of 4 to 12 carbons.
- [0041] Embodiment 6. The oil composition of any of the above embodiments, wherein the one or more calcium alkylnaphthalene sulfonates comprise calcium dinonylnaphthalene sulfonate.
- [0042] Embodiment 7. The oil composition of any of the above embodiments, wherein the one or more base oils comprise a Group I base oil, a Group II base oil, a polyalphaolefin base oil, or a combination thereof.
- [0043] Embodiment 8. The oil composition of any of the above embodiments, wherein the oil composition comprises a viscosity index of 50 or more, or wherein the oil composition comprises a viscosity index of 200 or less, or a combination thereof.
- [0044] Embodiment 9. The oil composition of any of the above embodiments, wherein the oil composition comprises a viscosity index of 70 to 130.
- [0045] Embodiment 10. The oil composition of any of the above embodiments, wherein the oil composition comprises a demulsification time according to ASTM D1401 at 54°C that is less than or equal to a demulsification time according to ASTM D1401 at 82°C.
- [0046] Embodiment 11. A method for lubricating a system, comprising: using an oil composition according to any of Embodiments 1 to 10 as a circulating oil, lubricant, or a combination thereof for a system comprising a circulating oil system, a turbine, a gear box, a blower, a pump, or a combination thereof.
- [0047] Embodiment 12. The method of Embodiment 11, wherein the oil composition is used as a circulating oil, a lubricant, or a combination thereof at a temperature of -20°C to 100°C.
- [0048] Embodiment 13. The method of Embodiment 11 or 12, wherein the oil composition is used as a circulating oil, a lubricant, or a combination thereof at a temperature of -20°C to 55°C.
- [0049] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other

- 13 -

modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

[0050] The present invention has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

# **CLAIMS:**

- 1. An industrial oil or lubricating oil composition, comprising: 0.30 wt% to 0.75 wt% of one or more calcium alkylnaphthalene sulfonates; and one or more base oils, the oil composition comprising a kinematic viscosity at 40°C of 130 cSt to 1000 cSt.
- 2. The oil composition of claim 1, wherein the oil composition comprises 0.30 wt% to 0.48 wt% of the one or more calcium alkylnaphthalene sulfonates.
- 3. The oil composition of any of the above claims, wherein each calcium alkylnaphthalene sulfonate comprises one or more alkyl side chains, the one or more alkyl side chains comprising a total length of 8 to 24 carbons.
- 4. The oil composition of any of the above claims, wherein the one or more calcium alkylnaphthalene sulfonates comprise one or more calcium dialkylnaphthalene sulfonates.
- 5. The oil composition of claim 4, wherein the one or more calcium dialkylnaphthalene sulfonate comprise alkyl side chains having a length of 4 to 12 carbons.
- 6. The oil composition of any of the above claims, wherein the one or more calcium alkylnaphthalene sulfonates comprise calcium dinonylnaphthalene sulfonate.
- 7. The oil composition of any of the above claims, wherein the one or more base oils comprise a Group I base oil, a Group II base oil, a polyalphaolefin base oil, or a combination thereof.
- 8. The oil composition of any of the above claims, wherein the oil composition comprises a viscosity index of 50 or more, or wherein the oil composition comprises a viscosity index of 200 or less, or a combination thereof.
- 9. The oil composition of any of the above claims, wherein the oil composition comprises a viscosity index of 70 to 130.
- 10. The oil composition of any of the above claims, wherein the oil composition comprises a demulsification time according to ASTM D1401 at 54°C that is less than or equal to a demulsification time according to ASTM D1401 at 82°C.
- 11. A method for lubricating a system, comprising: using an oil composition according to any of claims 1 to 10 as a circulating oil, lubricant, or a combination thereof for a system comprising a circulating oil system, a turbine, a gear box, a blower, a pump, or a combination thereof.

- 12. The method of claim 11, wherein the oil composition is used as a circulating oil, a lubricant, or a combination thereof at a temperature of -20°C to 100°C.
- 13. The method of claim 11 or 12, wherein the oil composition is used as a circulating oil, a lubricant, or a combination thereof at a temperature of -20°C to 55°C.

### INTERNATIONAL SEARCH REPORT

International application No

PCT/US2021/047444

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10M135/10

ADD. C10N20/02

C10N30/02

C10N40/02

C10N40/04

C10N40/12

According to International Patent Classification (IPC) or to both national classification and IPC

#### **B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C10M C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, WPI Data

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Calegory	Citation of document, with indication, where appropriate, of the relevant passages	nelevani (o ciain No.
x	WO 96/35765 A1 (EXXON RESEARCH ENGINEERING	1,3-12
	CO [US]; STADTMILLER WILLIAM H [US])	,
	14 November 1996 (1996-11-14)	
	page 1, paragraph 1	
	page 2, paragraph 2 - page 6, paragraph 1	
	claims; examples	
x	US 2007/238626 A1 (BARBER ALLAN [GB])	1-13
	11 October 2007 (2007-10-11)	
	paragraph [0001]	
	paragraph [0064] - paragraph [0065]	
	paragraph [0095]	
	claims; examples	
X	CN 103 571 577 B (CHINA PETROLEUM &	1-13
	CHEMICAL) 30 September 2015 (2015-09-30)	
	paragraphs [0032], [0038]	
	claims; examples	
	,	

	-/
Further documents are listed in the continuation of Box C.	X See patent family annex.
Special categories of cited documents :  "A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date  "L" document which may throw doubts on priority claim(s) or which is	"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means	"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report
5 May 2022	13/05/2022
Name and mailing address of the ISA/  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040,  Fax: (+31-70) 340-3016	Authorized officer  Elflein, Eleonore

# **INTERNATIONAL SEARCH REPORT**

International application No
PCT/US2021/047444

		101,052021,047444	
C(Continua	tion). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	
A	US 9 090 850 B1 (EDWARDS DAVID RYAN [US] ET AL) 28 July 2015 (2015-07-28) the whole document	1-13	
A		1-13	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2021/047444

cited	in search report		date		member(s)		date
WO	9635765	A1	14-11-1996	NON	E		
US	2007238626	<b>A1</b>	11-10-2007	CA	2648720	A1	18-10-2007
				CN	101432406	A	13-05-2009
				EP	2010633	A1	07-01-2009
				JP	5335665	B2	06-11-2013
				JP	2009533493	A	17-09-2009
				SG	170833	A1	30-05-201
				US	2007238626	A1	11-10-200
				US	2011065617	A1	17-03-201
				WO	2007117877	A1	18-10-200
CN	103571577	В	30-09-2015	NON	E		
us	9090850	в1	28-07-2015	CN	105198924	A	30-12-201!
				EP	2957624	A1	23-12-201
				JP	5925942	B2	25-05-201
				JP	2016003232	A	12-01-201
				KR	20150146441	A	31-12-201
				US	9090850	в1	28-07-201
	 3764533		 09-10-1973	NON			