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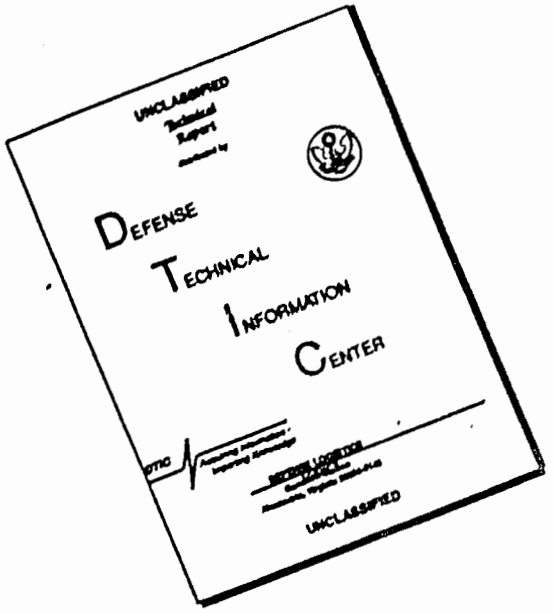

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Amphoteric Surfactants in Alkaline Cleaners

Report No. CCL # 34

Ordnance Project No. TB4-006A

D. A. Project No. 593-25-005

Author A. Mankowich

Date 30 October 1957

ABERDEEN PROVING GROUND
MARYLAND

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Report Number CCL # 34

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AMPHOTERIC SURFACTANTS IN ALKALINE CLEANERS

BY

A. Mankowich

30 October 1957

Contract No. - - -

OCO, R and D Branch Project No.
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Department of the Army Project
No. 593-25-005

Coating and Chemical Laboratory
Aberdeen Proving Ground
Maryland

Unclassified

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ABSTRACT

The object of this study was to explore the detergency and physical characteristics of soak alkaline cleaning compounds containing amphoteric surfactants; to determine whether such compounds could be developed that would be satisfactory Fed. Spec. P-C-436a cleaners.

Using the test procedures of P-C-436a, an investigation was make of alkaline cleaners containing amphoteric surfactants of the quaternary imidazolium hydroxide type.

Compounds containing the amphoteric surfactant as the only additive were ineffective asphalt removers. Good asphalt and mineral oil detergency was obtained from developed cleaners containing specific amounts of the undecyl or coconut oil amphoteric combined with specific amounts of an alkyl aryl sulphonate, or with nonionics of the alkyl aryl polyethylene glycol ether, alkyl polyethylene glycol ether or alkyl polyethylene glycol thioether types. The alkali-heat stability of such cleaners was good. Granular, free-flowing formulations were prepared, complying with the detergent and surface tension requirements of P-C-436a.

It is recommended that the developed cleaners be subjected to a field test at an Ordnance Depot.

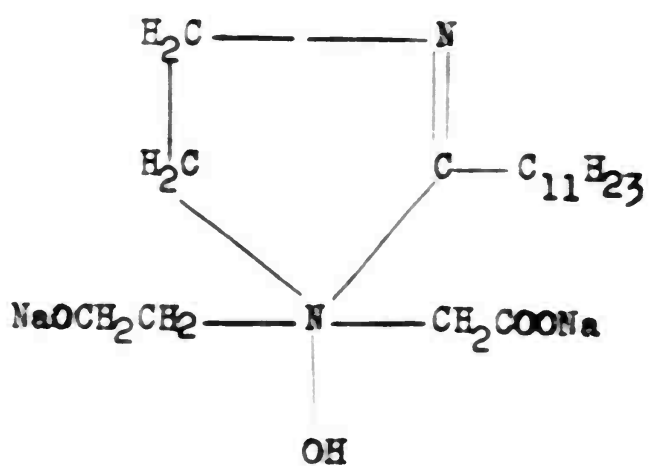
I INTRODUCTION

The Office, Chief of Ordnance, directed Aberdeen Proving Ground, Md., reference OO 438/815, APG 438/432, dated 12 September 1946, to review Ordnance Tentative Specification TAC-ES-No. 382b, Amendment 1, "Compound, Cleaning and Paint Stripping, Metal or Wood Surfaces, Alkali-Type", for the purpose of revision. Subsequent research led to the promulgation 15 June 1949 of Tentative Specification AXS-1849, "Compound, Cleaning, Alkali-Type", which was reissued 19 February 1952 as Interim Federal Specification P-C-436(Army-Ord).

By RAD, ORDTB-3-3228, dated 1 July 1952, the Office, Chief of Ordnance, directed Aberdeen Proving Ground, Md., to continue to evaluate, improve and/or develop cleaning materials for Ordnance application, obtain performance limits, and improve or develop test methods. Amendment 1 to Specification P-C-436 (Army-Ord) was issued 2 July 1953, covering deletion of the tar cleaning requirement and inclusion of a surface tension requirement. On 23 June 1954, Federal Specification P-C-436a, "Cleaning Compound, Alkali Type", superseded Int. Fed. Spec. P-C-436(Army-Ord).

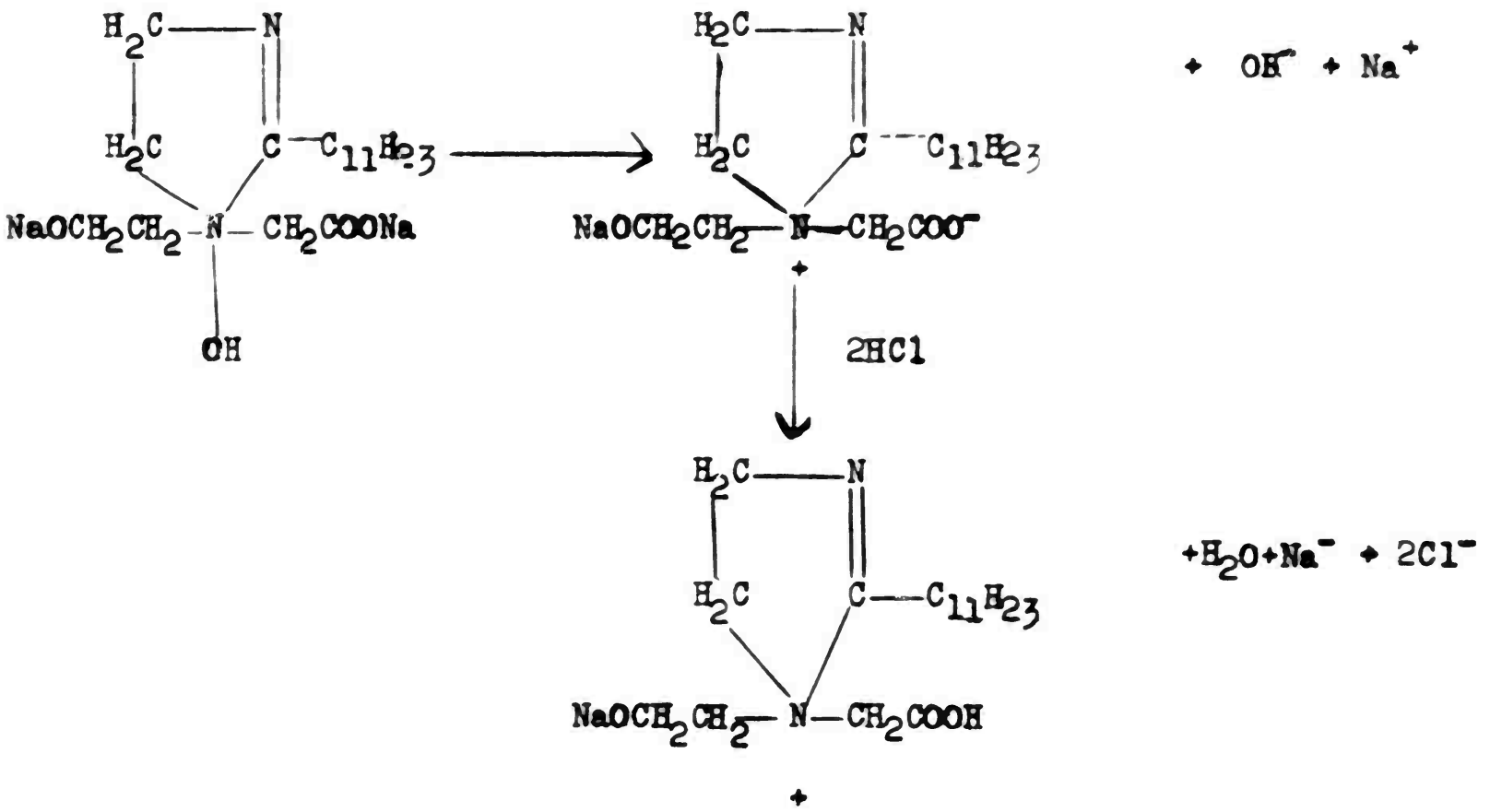
Subsequent investigations of alkaline cleaners in this laboratory (1,2) have covered studies of compounds containing various types and combinations of poly oxyalkylene diol nonionic agents. Formulations were developed whose asphalt detergency was superior to that of Specification P-C-436a cleaners. Such formulations also possessed excellent tar cleaning ability. Their high boundary tension values have been a disadvantage from the standpoint of the surface tension "policing" test of the specification. From all other viewpoints, the poly-oxyalkylene diol compounds were satisfactory as P-C-436a cleaners.

In this investigation, the studies of alkaline cleaners have been extended to compounds containing amphoteric surfactants of the quaternary imidazolium hydroxide type, the chief purpose being to determine whether compounds could be developed that would be satisfactory P-C-436a cleaners. The outstanding characteristic of these relatively new agents is that they behave anionically in alkaline solution and cationically in acid solution. They possess good stability to alakli and hard water components, and compatibility with electrolytes, alkalis and other types of surfactants. Their structure is illustrated by the following formula:

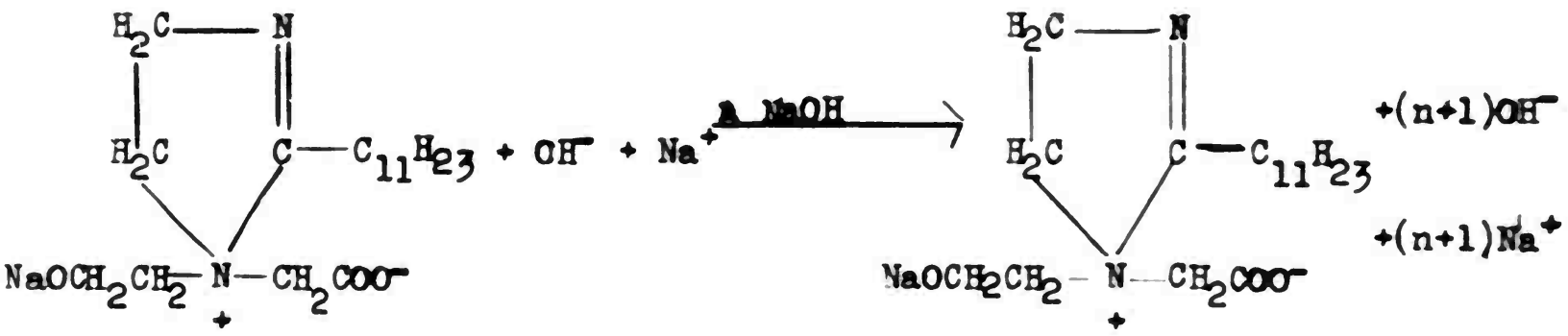


This agent is 1-(2-sodium acetato) 1-(2-sodium ethylato) 2-undecyl 4,5-dihydroimidazolium hydroxide.

The foregoing formula reveals a positive quaternary group and a negative carboxyl group. In acid solution, the following reaction takes place:



The electronically-bonded hydroxyl ion of the surfactant is neutralized. In addition, the carboxyl (sodium acetato) group forms a substituted acetic acid. Since the latter is essentially unionized in acid solution, the net charge on the surfactant is positive, and it will react cationically. In alkaline solution, the situation is as follows:



Since the mobility of the hydroxyl ion is approximately four times that of the sodium ion (3), the charge on the quaternary group will tend to be more nearly neutralized by its surrounding hydroxyl ions than the charge on the carboxyl group is by its surrounding sodium ions. Hence, the anionic carboxyl group is predominant, and the surfactant reacts anionically.

II DETAILS OF TEST

A. Test Methods

Test methods used in this investigation are those given in Federal Specification P-C-436a, with the exception that the concentration of the cleaning solutions was varied from 7.5 to 8.0 percent as noted, instead of

using the specified 7.5 percent.

Compounds covered by P-C-436a are capable of 100% asphalt removal in not more than 21 minutes in the standardized cleaning efficiency test. In the studies reported herein, the asphalt cleaning time was 21 minutes unless completeness of soil removal was observed prior to that time.

B. Results

1. Amphoteric-Alkyl Aryl Polyethylene Glycol Ether Cleaners (Tables II, III)

Compounds containing only the amphoteric surfactant were poor asphalt removers.

Excellent asphalt detergency was obtained from compounds containing 11% of the undecyl amphoteric combined with 2.0-5.7% of iso-octylphenyl nonaethylene glycol ether (IOPNG). With cleaners containing 6.0% of the latter, the undecyl amphoteric content could be reduced to 9.0% with retention of good asphalt-removing properties; a further reduction of the amphoteric content to 7.5% gave only border-line detergency.

Good asphalt detergency was given also by combinations of the coconut oil amphoteric and IOPNG; namely, 3.0-9.8% IOPNG with 11% of the coconut oil amphoteric. Reducing the latter to 11.7% in a compound containing 5.8% IOPNG resulted in the loss of asphalt detergency. The detergency of the coconut oil amphoteric combinations was not as good as that of the undecyl amphoteric mixtures with IOPNG.

The nonyl, tridecyl and heptadecyl amphoteric mixtures with IOPNG possessed no asphalt-removing ability.

2. Amphoteric-Alkyl Aryl Sulphonate Cleaners (Tables IV, V)

Cleaners containing combinations of 8.0-11% of the undecyl amphoteric and 6.0% sodium dodecyl benzene sulphonate (SDBS) were excellent asphalt detergents. Decreasing the undecyl amphoteric content to 7.0% resulted in border-line detergency. A 9.0% coconut oil amphoteric - 6.0% SDBS mixture gave good asphalt cleaning, but a 11% cocoonut oil-6.0% SDBS mixture had no asphalt-removing ability.

When an equivalent amount of 40% active, alkyl aryl sulphonate was substituted for the SDBS in the 9.0% cocoonut oil amphoteric -6.0% SDBS combination, the resultant cleaner had no asphalt detergency.

3. Amphoteric-Miscellaneous Nonionic Cleaners (Tables VI, VII)

Excellent asphalt detergency was obtained from a cleaner containing 11% of the undecyl amphoteric and 5.7% of an alkyl polyethylene glycol ether. Fair asphalt removal was given by a combination of 11% of the undecyl amphoteric plus 5.7-7.3% of an alkyl polyethylene glycol thioether. A polypropylene glycol (molecular weight ca 1025) in combination with the undecyl amphoteric possessed good asphalt detergency, but poor mineral oil cleaning properties.

The undecyl and coconut oil amphoterics (13-14% concentrations) in combination with liquid or solid oxyethylene-oxypropylene diols or a fatty acid alkanolamide (5.7% concentrations) were ineffective asphalt removers.

4. Amphoteric-Miscellaneous Anionic Cleaners (Tables VIII, IX)

Combinations of the undecyl or coconut oil amphoterics (9.0-14% concentrations) with a fatty acid soap, an alkyl sulphate, or an alkyl aryl polyether sulphonate (6.0% active concentrations) possessed no asphalt detergency.

5. Miscellaneous Tests, Amphoteric Cleaners

Developed compounds containing the undecyl and coconut oil amphoteric in combination with IOPNG, and which had previously shown good asphalt detergency, passed the granulation, surface tension and stability tests of P-C-436a.

6. Discussion

The low boundary tensions of the developed amphoteric formulations could make them of immediate utility provided they field test satisfactorily. Since they are controllable by the surface tension "policing" test of P-C-436a, the developed cleaners could be submitted for qualification and acceptance under the specification, and provide a new or alternate Standard Comparison Compound.

When combined with anionic SDBS or nonionic IOPNG, the undecyl amphoteric (a lauric acid derivative) imparted superior asphalt detergency to cleaning compounds over a wider concentration range (amphoteric) than the coconut oil amphoteric. The major constitutents of coconut oil are lauric acid (ca 46%) and myristic acid (ca 18%). Since the tridecyl amphoteric (the myristic acid derivative) was ineffective as an asphalt-cleaning synergist, the reason for the superiority of the undecyl amphoteric is obvious.

The undecyl (or cocoonut oil) amphoteric-sodium dodecyl benzene sulphonate mixtures are unique in that they are the only combinations of two anionic surfactants thus far discovered with the ability to impart asphalt detergency to an alkaline cleaner under the test conditions of P-C-436a. The P-C-436a cleaners and the polyoxyalkylene diol cleaners, as well as most of the amphoteric cleaning compounds developed in this investigation, consist of mixtures of anionic and nonionic surfactants.

III REFERENCES

1. Engineering Laboratories Report No. 7, August 1955

2. Engineering Laboratories Report No. 39, April 1956

3. H. S. Taylor "Treatise on Physical Chemistry", Vol. I, page 540; 1925; D. Van Nostrant Co., New York, N. Y.

AUTHOR:

A. Mankowich

A. Mankowich, Chemist
Chemical Cleaning and Corrosion Branch

REVIEWED BY:

M. Rosenfeld

Dr. M. Rosenfeld, Chief
Chemical Cleaning and Corrosion Branch

APPROVED BY:

C F Pickett

Dr. C. F. PICKETT, Director
Coating and Chemical Laboratory

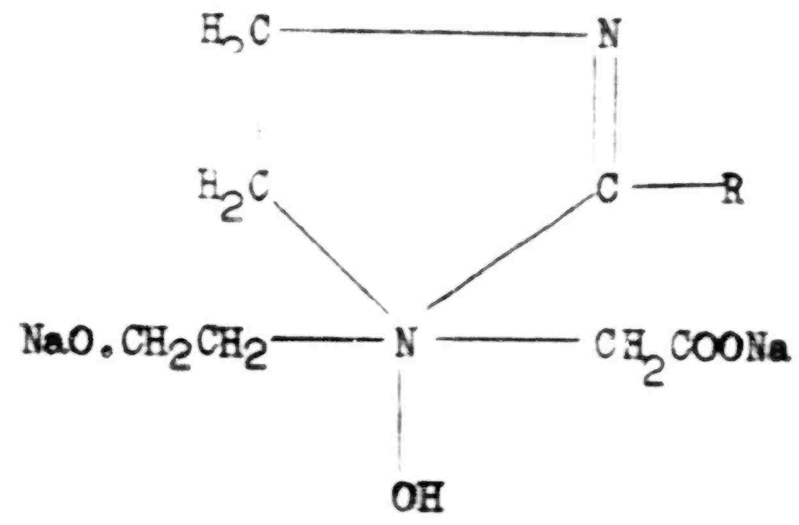
APPENDIX

TABLES

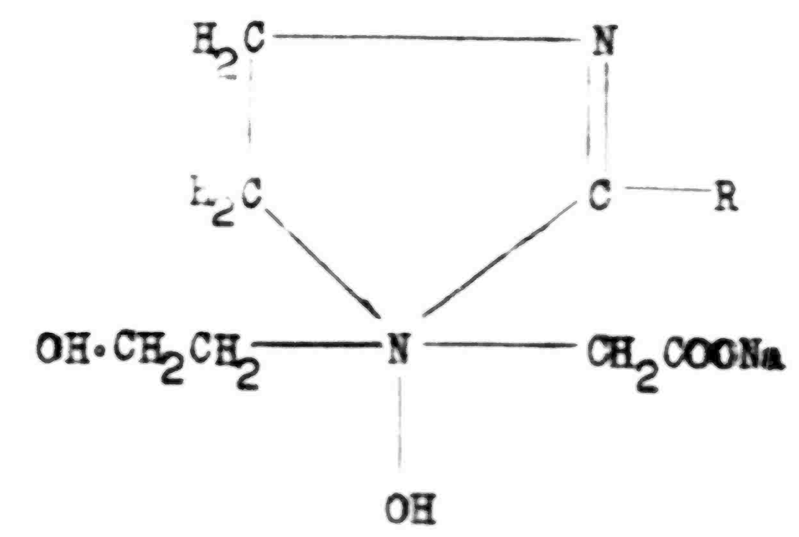
TABLE I

Amphoteric Surfactants

General Formula for Surfactants 2, 3 and 4:



General Formula for Surfactants 1 and 5:



R	Derivative	Amphoteric Surfactant No.
C_9H_{19}	Capric acid	1
$C_{11}H_{23}$	Lauric acid	2
R_1	Coconut Oil	3
$C_{13}H_{27}$	Myristic acid	4
$C_{17}H_{35}$	Stearic acid	5

NOTE: All above surfactants are 45% active.

TABLE II

Amphoteric --- Alkyl Aryl Polyethylene Glycol Ether Cleaners

Cleaner	Amphoteric Surfactant	% Solution, grams/100cc	Composition --- % by Weight				
			$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Other Surfactants*
A	3	7.5	38.8	13.5	37.7	10.0	None
B	2	7.5	34.5	12.0	33.5	20.0	None
C	3	7.5	36.7	12.8	33.5	9.0	6.0
D	3	7.7	35.6	12.4	34.5	11.7	5.8
E	3	8.0	34.6	12.1	33.5	14.1	5.7
F	3	8.0	35.8	12.5	34.7	14.0	3.0
G	2	8.0	34.6	12.1	33.5	14.1	5.7
H	2	8.0	36.4	12.7	35.4	14.0	1.5
I	2	8.0	36.2	12.6	35.2	14.0	2.0
J	2	7.5	36.7	12.8	35.5	9.0	6.0
K	2	7.5	37.3	13.0	36.2	7.5	6.0
L	1	8.0	34.6	12.1	33.5	14.1	5.7
M	4	8.0	34.6	12.1	33.5	14.1	5.7
N	5	8.0	34.6	12.1	33.5	14.1	5.7
O	3	7.9	32.8	11.4	31.9	14.3	9.8

* Isooctylphenyl nonaethylene glycol ether, 100.% active

TABLE III

Detergency of Amphoteric Alkyl Aryl Polyethylene Glycol Ether Cleaners

Cleaner	Asphalt Soil Detergency	Remarks
A	Heavy residue on 1/5 to 1/3 panel areas	Mineral Oil detergency good
B	25. mg heavy residue	" " " "
C	50-138 mg heavy residue	" " " "
D	19 mg heavy residue	" " " "
E	1-2 specks left-----100% removal	" " " "
F	1 speck - 3mg left -----good to fair removal	" " " "
G	100% removal in 15-21 minutes	" " " "
H	5 mg residue ----- border-line detergency	" " " "
I	100% removal	" " " "
J	100% removal	" " " "
K	1.5-8 mg residue ----- border-line detergency	" " " "
L	92 mg residue	
M	9 mg residue - poor detergency	
N	Zero removal - poor detergency	
O	0.6-2.5 mg residue ----- good to fair removal	" " " "

NOTE: Asphalt cleaning time - 21 minutes, unless otherwise noted.

TABLE IV

Amphoteric - Alkyl Aryl Sulphonate Cleaners

Cleaner	Amphoteric Surfactant	% Solution, grams/100cc	Composition by Weight				
			$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Alkyl Aryl Sulphonate
P	3	7.5	36.7	12.8	35.[illegible]	9.0	6.0*
Q	3	8.0	34.5	12.0	33.5	14.0	6.0*
R	2	7.5	36.7	12.8	35.5	9.0	6.0*
S	2	8.0	34.5	12.0	33.5	14.0	6.0*
T	2	7.5	37.5	13.1	36.4	7.0	6.0*
U	2	7.5	37.1	12.9	36.0	8.0	6.0*
V	3	7.8	33.2	11.5	32.2	8.7	14.4**
W	3	8.0	30.7	10.7	29.6	14.0	15.0**
X	2	7.5	36.5	12.8	35.4	9.0	6.3***

* - 100% active, sodium dodecyl benzene sulphonate

** - 40% active, sodium alkyl benzene sulphonate; alkyl groups include 10 to 20 carbons

*** - 92% active, sodium alkyl benzene sulphonate; alkyl groups include 10 to 20 carbons

TABLE V

Detergency of Amphoteric - Alkyl Aryl Sulphonate Cleaners

Cleaner	Asphalt Soil Detergency
P	1-2 specks left ----- 100% removal
Q	81 mg heavy residue
R	100% removal in 18-21 minutes
S	1 speck - 0.5 mg residue ----- good detergency
T	1.2 - 31 mg residue ----- border-line detergency
U	100% removal
V	80 mg heavy residue - 1/3 panel area
W	37 mg heavy residue
X	1-2 mg residue ----- good to fair removal

TABLE VI

Amphoteric - Miscellaneous Nonionic Cleaners

Cleaner	Amphoteric Surfactant	% Solution, grams/100cc	Composition - % by Weight				
			$Na_2SiO_3.5H_2O$	$NaH_2PO_4.H_2O$	$Na_3PO_4.12H_2O$	Amphoteric	Nonionic
AA	3	7.5	35.0	12.0	34.0	13.2	5.8*
BB	2	8.0	34.6	12.1	33.5	14.1	5.7**
CC	2	8.0	34.6	12.1	33.5	14.1	5.7***
DD	2	8.0	34.6	12.1	33.5	14.1	5.7▲
EE	2	8.0	34.6	12.1	33.5	14.1	5.7●
FF	2	8.0	34.3	11.9	33.2	14.1	6.5●
GG	2	8.0	34.0	11.7	32.9	14.1	7.3●
HH	2	8.0	34.6	12.1	33.5	14.1	5.7✦ &

* - 100% active, liquid oxyethylene - oxypropylene diol, approximately 2,000 molecular weight

** - 100% active, solid oxyethylene - oxypropylene diol, approximately 7,500 molecular weight

*** - 100% active, polypropylene glycol - 1025

▲ - 100% active, tridecyl dodecaethylene glycol ether

● - 95% active, t-dodecyl nonaethylene glycol thioether

✦ - 100% active, lauric diethanolamide

TABLE VII

Detergency of Amphoteric - Miscellaneous Nonionic Cleaners

Cleaner	Asphalt Soil Detergency	Remarks
AA	Heavy residue on 1/2 panel area	
BB	106 mg heavy residue	
CC	0.5 - 1 mg residue ----- good removal	Poor mineral oil detergency
DD	1-2 specks left ----- 100% removal	
EE	2 mg residue ----- fair removal	
FF	4 mg residue ----- fair removal	
GG	2 mg residue ----- fair removal	
HH	1.5 - 37 mg residue ----- poor removal	

TABLE VIII

Amphoteric - Miscellaneous Anionic Cleaners

Cleaner	Amphoteric Surfactant	% Solution grams/100cc	Composition - % by weight				
			$Na_2SiO_3.5H_2O$	$NaH_2PO_4.H_2O$	$Na_3PO_4.12H_2O$	Amphoteric	Anionic
II	3	7.5	36.7	12.8	35.5	9.0	6.0•
JJ	2	7.5	36.7	12.8	35.5	9.0	6.0▲
KK	2	7.5	36.7	12.8	35.5	9.0	6.0♦
LL	3	8.0	30.7	10.7	29.6	14.0	15.0●

• - Sodium oleate, USP

▲ - 95% active, sodium lauryl sulphate

♦ - 100% active, sodium dibutylphenyl phenol disulphonate

● - 28% active, sodium alkyl arylpolyethylene glycol ether sulphonate

TABLE IX

Detergency of Amphoteric - Miscellaneous Anionic Cleaners

Cleaner	Asphalt Soil Detergency
II	41 mg heavy residue ----- poor
JJ	41-55 mg heavy residue ----- poor
KK	4-83 mg heavy residue ----- poor
LL	49 mg heavy residue ----- poor

TABLE X

Miscellaneous Tests - Amphoteric Cleaners

Cleaner	Spec. P-C-436a Test	Results
G	Granulation	granular, free flowing ---- passes
G	Surface tension	32.1 dynes per cm. ---- passes
O	Stability	Asphalt detergency ---- passes

NOTES:

Surface tension ---- in 0.05% solution at 25°C.

Stability ---- standard detergency test run on solution that has been boiled 40 hours.

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REPLY TO
ATTENTION OF

05 NOV 2012

RDCB-DPC-RS

MEMORANDUM THRU Director, Edgewood Chemical Biological Center, (ECBC) (RDCB-D), 5183 Blackhawk Road, Aberdeen Proving Ground, MD 21010-5424

FOR Office of the Chief Counsel, US Army Research, Development and Engineering Command (RDECOM) (AMSRD-CCF/Ms. Kelly Knapp), 3071 Aberdeen Boulevard, Aberdeen Proving Ground, MD 21005-5424

SUBJECT: Operations Security/Freedom of Information Act (FOIA) Review Request

1. The purpose of this memorandum is to recommend the release of information in regard to RDECOM FOIA Request, FA-13-0001.

2. On 2 October 2012, the Edgewood Chemical Biological Center (ECBC) received RDECOM FOIA Tasker #FA-13-0001. The request originated from the Defense Technical Information Center (DTIC) at Fort Belvoir, VA.

3. The following documents were reviewed by Subject Matter Experts from ECBC and deemed appropriate for both downgrade and release:

a. AD 149572, Amphoteric Surfactants in Alkaline Cleaners, 30 Oct 57.

b. AD 206020, Low Surfactant Content Amphoteric Cleaners, 13 Aug 1958.

c. AD 249437, Amino Carbolic Amphoteric Surfactants in Alkaline Cleaners, 9 Nov 1960.

4. The ECBC point of contact for this action is Mr. Ronald L. Stafford, 410-436-6810 or ronald.l.stafford.civ@mail.mil.

JUNE K. SELLERS
Security Manager