

Oct. 30, 1973

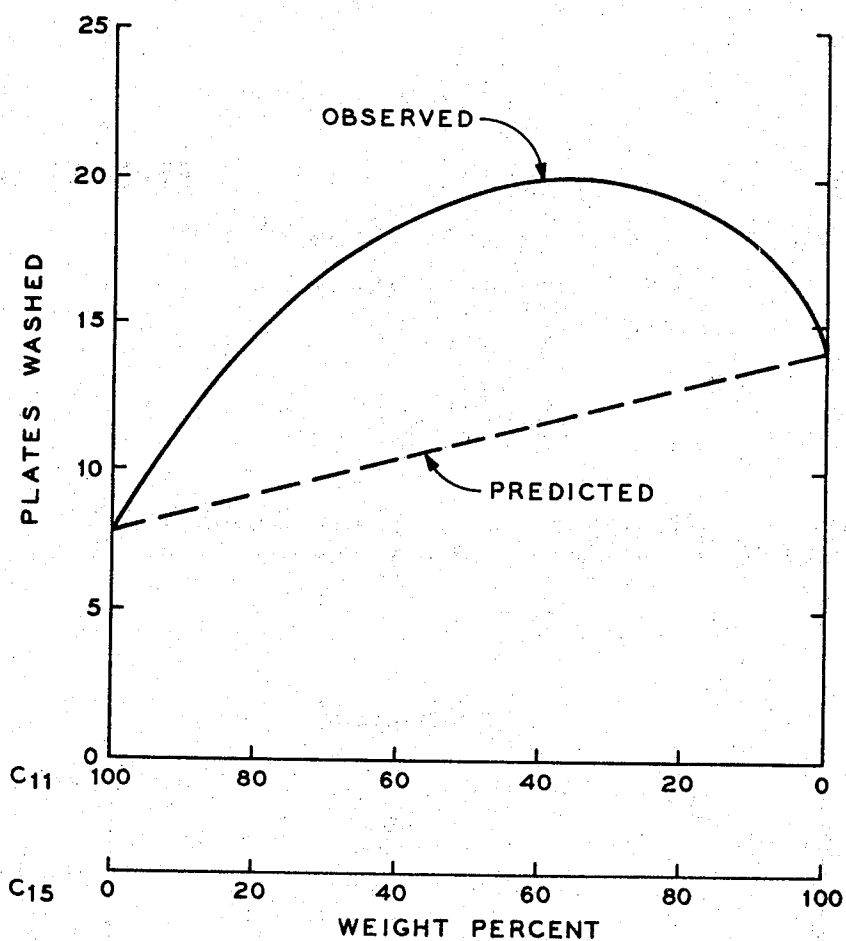
A. E. STRAUS

3,769,243

LINEAR ALKYL BENZENE SULFONATE DETERGENT COMPOSITIONS

Original Filed June 11, 1969

SYNERGISM IN MIXTURES OF SECONDARY C<sub>11</sub> AND  
INTERNAL C<sub>15</sub> SULFONATED PHENYL-N-ALKANES



1

3,769,243

## LINEAR ALKYL BENZENE SULFONATE DETERGENT COMPOSITIONS

Alan E. Straus, El Cerrito, Calif., assignor to Chevron  
Research Company, San Francisco, Calif.

Original application June 11, 1969, Ser. No. 832,293, now  
Patent No. 3,647,899. Divided and this application May  
27, 1971, Ser. No. 147,702

Int. Cl. C11d 1/22, 3/065

U.S. Cl. 252-558

3 Claims 10

### ABSTRACT OF THE DISCLOSURE

Sulfonated derivatives of novel detergent alkylate compositions exhibiting superior synergistic detergent characteristics comprise mixtures of secondary C<sub>11</sub> and C<sub>15</sub> sulfonated phenyl-n-alkanes in a weight ratio of from 1:10 to about 4:1, respectively.

This application is a division of applicant's co-pending application Ser. No. 832,293, filed June 11, 1969, now Pat. No. 3,647,899.

### BACKGROUND OF THE INVENTION

#### Field of the invention

This invention relates to the field of synthetic detergent compositions and, more particularly, to biodegradable, synergistic mixtures of sulfonated phenyl-n-alkane detergent compositions.

#### Prior art

In recent years, a significant emphasis has been placed upon finding suitable detergent compositions which do not deleteriously affect the ecological balance of water bodies used for receiving treated or untreated municipal and industrial waste. As a result, biodegradable sulfonated phenyl-n-alkanes have been substituted on a large commercial basis for the less biodegradable branched-chain alkylbenzene sulfonates. Much effort and research have been devoted to developing sulfonated phenyl-n-alkane mixtures approaching or equalling the high detergent efficiency of the alkylbenzene sulfonates. For example, U.S. 3,349,141 and 3,487,023 disclose detergent alkylate and sulfonated detergent alkylate compounds which exhibit high deterative characteristics comprising mixtures of secondary phenyl-n-alkanes containing 11 to 14 carbon atoms in the alkane portion of the molecule. In particular, these mixtures are low in 2- and 3-phenyl-n-alkane isomers which impair deterative effectiveness. As indicated in the aforementioned patent, it is known that the C<sub>11</sub> sulfonated phenyl-n-alkanes show very poor detergency. In addition, heretofore the C<sub>15</sub> sulfonated phenyl-n-alkanes have not shown acceptable deterative characteristics. In fact, most references in the art prefer and are limited to mixtures of C<sub>12-14</sub> sulfonated phenyl-n-alkanes.

### SUMMARY OF THE INVENTION

Surprisingly, we have now found that mixtures of secondary C<sub>11</sub> and C<sub>15</sub> sulfonated phenyl-n-alkanes exhibit excellent synergistic detergency which is not expected or predictable from their individual deterative characteristics. In particular, the novel compositions of the present invention comprise mixtures of sulfonated phenyl-n-alkanes containing secondary C<sub>11</sub> and C<sub>15</sub> sulfonated phenyl-n-alkanes in a weight ratio of from about 1:10 to 4:1 and, preferably, 1:4 to 1.5:1. More preferably, the C<sub>15</sub> sulfonated phenyl-n-alkane portion is low in the 2- and 3-phenyl isomers.

In addition, the C<sub>11</sub> and C<sub>15</sub> components may be combined within the described ratio with other satisfactory

2

sulfonated phenyl-n-alkanes detergents, with no adverse effect on the overall detergency. That is, for example, an excellent detergent composition may contain 30 percent of secondary C<sub>11</sub> and C<sub>15</sub> sulfonated phenyl-n-alkanes in the proper proportions, and 70 percent of a mixture of C<sub>12-14</sub> sulfonated phenyl-n-alkanes low in the 2- and 3-phenyl isomers.

### DESCRIPTION OF DRAWING

The figure graphically depicts the observed synergistic effect of mixtures of C<sub>11</sub> and C<sub>15</sub> sulfonated phenyl-n-alkanes as compared to the predicted effect.

### DETAILED DESCRIPTION OF INVENTION

The secondary phenyl-n-alkanes utilized in the present invention may be prepared by conventional methods as known in the art. These methods include the alkylation of benzene or its derivatives, such as toluene and xylene, with n-alkenes or n-haloalkanes containing from 11 to 15 or more carbon atoms. The n-alkenes or n-haloalkanes may be derived from distillate cracking or wax cracking, catalytic dehydrogenation of n-alkanes, chlorination-dehydrochlorination of n-alkanes, ethylene polymerization and chlorination of n-alkanes. In addition, the raw materials from which the straight-chain stock is to be derived may be subjected to iso-normal separation processes, such as molecular sieves, and urea clathration to produce a more linear product than can otherwise be obtained.

After alkylation of the benzene ring or its derivative, the aromatic portion is sulfonated by known methods with such agents as chlorosulfonic acid, sulfur trioxide, and oleum, etc.

The mixtures of secondary C<sub>11</sub> and C<sub>15</sub> sulfonated phenyl-n-alkanes may be directly used as the active ingredient to form excellent detergent compositions, or may be beneficially combined with mixtures of other sulfonated phenyl-n-alkanes. In the latter use where the other sulfonated phenyl-n-alkanes are superior in dishwashing ability to the secondary C<sub>11</sub> and C<sub>15</sub> mixture, the C<sub>11</sub> and C<sub>15</sub> component may range from as much as 30 to 40 percent and, preferably, from 5 to 20 percent by weight of the active ingredient of the detergent composition. However, where the other sulfonated phenyl-n-alkanes are equivalent or less in dishwashing ability, there is no limitation on the amount of the C<sub>11</sub> and C<sub>15</sub> utilized. Preferably, the C<sub>11</sub> and C<sub>15</sub> mixtures are combined with C<sub>12-14</sub> mixtures low in the 2- and 3-phenyl isomers. In effect, the incorporation of C<sub>11</sub> and C<sub>15</sub> mixtures into other sulfonated phenyl-n-alkanes often increases the average molecular weight, broadens the acceptable range of usable phenyl-n-alkanes and, accordingly, provides significant economic advantages and incentives.

The secondary C<sub>11</sub> sulfonated phenyl-n-alkane component may comprise isomers containing internal phenyl attachment (4-, 5-, and 6-isomers), end phenyl attachment (2-, and 3-isomers) or a distribution over the whole isomer range. All distributions of the C<sub>11</sub> isomers exhibited the excellent synergistic effect upon combination with the C<sub>15</sub> compound.

The C<sub>15</sub> sulfonated phenyl-n-alkanes also showed excellent synergism for the end phenyl attachment (2-, and 3-isomers) and for distribution over the whole range of isomers. Surprisingly, however, the internal phenyl attachment (5-, 6-, 7-, and 8-isomers) exhibited substantially increased synergism over the end and whole isomer distributions. In general, mixtures of C<sub>15</sub> sulfonated phenyl-n-alkanes containing at least 70% by weight of internal isomers and preferably from 80 to 90% showed this increased synergism.

In general, the ratio of  $C_{11}$  to  $C_{15}$  sulfonated phenyl-n-alkanes may vary from about 1:10 to about 4:1, respectively. Preferably, however, the ratio ranges from 1:4 to about 1.5:1.

Additional compatible ingredients may be incorporated into the detergent compositions prepared in accordance with the present invention to enhance their detergent properties. Such ingredients may include, but are not limited to, anticorrosion, anti-redeposition, belaching and sequestering agents, optical whiteners and certain organic and inorganic alkali and alkaline earth salts, such as inorganic phosphates, sulfates, carbonates or borates, and the organic salts, such as sulfosuccinates, xylene sulfonates, and the alkali metal salts of polycarboxylic acids; e.g., trisodium salt of nitrilo acetic acid, tetrasodium salt of ethylenediaminetetraacetic acid, etc.; and the sodium salt of the copolymer of maleic anhydride and ethylene. The appropriate quantities and compositions of these additives, agents and builders are well described in the art.

An effective means for evaluating the deterative characteristics of detergent compositions is known as the "Hand Dishwashing Test" which is based on a procedure presented at the ASTM D-12 Subcommittee on Detergents, Mar. 10, 1949, New York, N.Y. The test measures, under simulated home washing conditions, the number of plates or dishes washed before the foam collapses. This test was utilized to evaluate the improved performance of the disclosed detergent compositions.

Detergent formulations were prepared from the sulfonated phenyl-n-alkane mixtures of the present invention, water and other ingredients. The formulations were adjusted until the percentage of sulfonated phenyl-n-alkanes equalled about 25 percent by weight of the total detergent formulation.

In the following examples, the concentrations employed

## EXAMPLE 1

A detergent formulation was prepared containing the following percentages of each ingredient, based on the total weight of the formulation:

Formulation, wt. percent	
50% $C_{11}$ +50% $C_{15}$ (internal)	24
Sulfonated phenyl-n-alkanes	40
Sodium tripolyphosphate	7
Sodium silicate	1
Carboxymethylcellulose	20
Sodium sulfate	8
Water	

The formation was tested and found effective in accordance with the "Hand Dishwashing Test" for a rating of 18 plates.

Example 2 is an analysis of the mass distribution of the side chains in the  $C_{11}$ - $C_{14}$  sulfonated phenyl-n-alkanes used in subsequent evaluation.

## EXAMPLE 2

## MASS DISTRIBUTION OF SIDE CHAINS

Mass distribution of side chains	Weight percent	Mole percent
< $C_{11}$ -----	1.4	1.6
$C_{11}$ -----	9.4	10.3
$C_{12}$ -----	32.8	33.9
$C_{13}$ -----	33.3	32.7
$C_{14}$ -----	22.7	21.1
$C_{15}$ -----	0.4	0.4
Total-----	100.0	100.0
Average molecular weight-----	254	254

Table I discloses the phenyl isomer distribution of the  $C_{11}$  and  $C_{15}$  alkylates of the present invention.

TABLE I.—ISOMER COMPOSITION OF  $C_{11}$  AND  $C_{15}$  ALKYLATES AND BLENDS

Example	Phenyl-n-alkanes	Straight-chain isomer distribution, wt. percent			
		5-phenyl through 8-phenyl	4-phenyl	3-phenyl	2-phenyl
3-----	$C_{11}$ -----	10	13	27	50
4-----	$C_{15}$ (internal) <sup>1</sup> -----	84	11	4	1
5-----	$C_{15}$ (end)-----	15	16	29	40
6-----	$C_{15}$ (whole) <sup>2</sup> -----	61	13	12	14
7-----	$C_{11}$ - $C_{14}$ <sup>3</sup> -----	45	16	16	23
8-----	80% $C_{11}$ - $C_{14}$ <sup>3</sup> plus 20% internal $C_{15}$ -----	52	15	14	19
9-----	80% $C_{11}$ - $C_{14}$ <sup>3</sup> plus 20% whole $C_{15}$ -----	48	16	15	21

<sup>1</sup> Contains 6%  $C_{14}$ .

<sup>2</sup> Two parts internal/one part end; contains 4%  $C_{14}$ .

<sup>3</sup> Sulfonated phenyl-n-alkane of Example 2.

in the "Hand Dishwashing Test" were 0.15 percent by weight of the total detergent formulation.

Example 1 illustrates a suitable detergent formulation prepared from the sulfonated phenyl-n-alkane mixtures of the present invention.

Table II illustrates the synergistic effect of the  $C_{11}$ / $C_{15}$  sulfonated phenyl-n-alkane blends of the present invention. It is noted that the synergistic effect for the  $C_{15}$  internal isomers in Example 15 is almost double that of the  $C_{15}$  whole isomers of Example 17.

TABLE II.—DISHWASHING PERFORMANCE OF 0.15 CONCENTRATIONS OF FORMULATIONS CONTAINING  $C_{11}$  AND  $C_{15}$  SULFONATED PHENYL-N-ALKANES (50 P.P.M.) <sup>1</sup>

Example	Sulfonated phenyl-n-alkanes	Number of plates washed		
		Measured	Pre-dicted (from graph)	Synergistic improvement
10-----	$C_{11}$ -----	8		
11-----	$C_{15}$ (internal)-----	14		
12-----	$C_{15}$ (end)-----	12		
13-----	$C_{15}$ (whole)-----	12		
14-----	$C_{11}$ / $C_{15}$ (internal) mixtures by weight:-----			
15-----	1:2-----	20	13	7
16-----	1:1-----	20	11	9
17-----	2:1 (whole), 1/1: $C_{11}$ / $C_{15}$ -----	17	10	7
18-----	( $C_{15}$ (whole), 1/1: $C_{11}$ / $C_{15}$ -----	15	10	5
19-----	$C_{11}$ - $C_{14}$ <sup>2</sup> -----	20		
20-----	80% $C_{11}$ - $C_{14}$ <sup>2</sup> plus 20% $C_{15}$ (internal)-----	20	18	2
21-----	80% $C_{11}$ - $C_{14}$ <sup>2</sup> plus 20% $C_{15}$ (whole)-----	18	18	0

NOTE.—See Table I for compositions:

<sup>1</sup> 24/40/7/1/20/8 formulation.

<sup>2</sup> Sulfonated phenyl-n-alkane of Example 2.

While the character of this invention has been described in detail with numerous examples, this has been done by way of illustration only and without limitation of the invention. It will be apparent to those skilled in the art that modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the following claims.

I claim:

1. A detergent composition the active ingredient of which consists of a mixture of from about 10 to 85 percent by weight of sulfonated secondary C<sub>11</sub> phenyl-n-alkanes and from about 15 to 90 percent by weight of sulfonated secondary C<sub>15</sub> phenyl-n-alkanes.

2. A detergent composition as in claim 1, wherein from 50 to 100 weight percent of the C<sub>15</sub> phenyl-n-alkanes are the 5-, 6-, 7- and 8-positional isomers.

3. A detergent composition as in claim 2, wherein the sulfonated C<sub>11</sub> phenyl-n-alkanes comprise from about 20 to 70 percent by weight of the detergent composition and

the sulfonated C<sub>15</sub> phenyl-n-alkanes comprise from about 30 to 80 percent by weight.

#### References Cited

##### UNITED STATES PATENTS

3,316,294	4/1967	Feighner et al. ....	260—505
3,320,174	5/1967	Rubinfeld .....	260—671 B X
3,349,141	10/1967	Sweeney .....	260—668
3,358,047	12/1967	Liston .....	260—668
3,487,023	12/1969	Sweeney .....	252—558
3,333,014	7/1967	Adams et al. ....	260—671 B

LEON D. ROSDOL, Primary Examiner

P. E. WILLIS, Assistant Examiner

U.S. Cl. X.R.

252—539