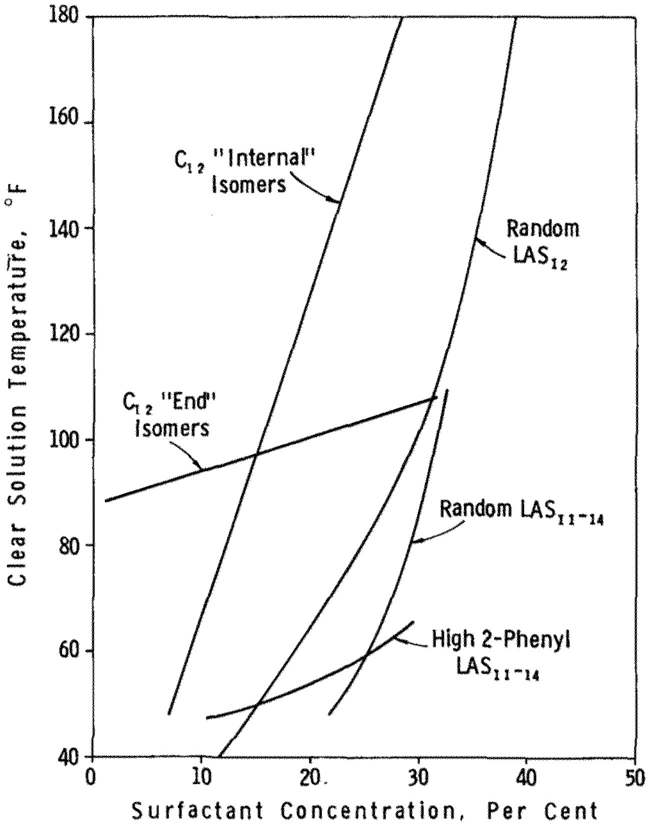

FIG. 14. Isomer effects on solubility (sodium salts).

machine foam, but the differences are not large enough to be noticeable in a wide-range product. For example, C_{11-14} random LAS and high 2-phenyl LAS whose 2-phenyl contents are ca. 18 and 32%, respectively, are compared in a 25/40/7/1/19/8 formula at the bottom of Table IV. There is no difference beyond experimental error between the two.

Solubility is also influenced by isomer distribution as shown in Figure 14. The C_{12} end isomers sulfonate has a very flat clear point curve reminiscent of a number of pure straight-chain surfactants (12). (Pure 2-phenyldodecane sulfonate itself has a curve ca. 10F higher.) The C_{12} internal isomers sulfonate which contains no 2-phenyl isomer has a very steep and straight clear point curve. The random C_{12} and C_{11-14} LAS which have low 2-phenyl contents (ca. 18%) are also steep but show a little tendency to curve over at low temp. The flattening out is quite pronounced with the high 2-phenyl LAS which contains about 32% 2-phenyl isomers. Therefore, increasing 2-phenyl content up to at least 32% increases room temp solubility.

LAS is basically equal to or better than PPABS, except in dishwashing foamability. The separate LAS isomers show a small advantage to the end attachment in detergency and washing machine foaming and a large advantage for the internal isomers in dishwashing foam tests. The latter effect appears large enough to be noticeable when the 2-phenyl content varies in commercial-type products.

ACKNOWLEDGMENTS

Helpful advice from R. House and J. D. Knight; preparation of the pure 2-phenylalkane sulfonates by E. D. Vessel; contributions to the performance testing by A. E. Straus and J. K. Foote; and general support from the California Chemical Co.

REFERENCES

1. Stayner, R. D., Soap Chem Specialties *37*, No. 3, 143 (1961); "Oronite's New Detergent Alkylate," Soap Chem. Specialties, p. 52, April 1960.
2. Gray F. W., J. F. Gerecht and I. J. Krems, J. Org. Chem. *20*, 511 (1955).
3. Gray, F. W., and I. J. Krems, *Ibid.* *26*, 209 (1961).
4. Baumgartner, F. N., Ind. Eng. Chem. *46*, 1349 (1954).
5. Koelbel, H., D. Klamann and P. Kurtzendoerfer, "Influence of Constitution on the Properties of Surface-Active Substances," 3rd International Conference of Surface Activity, Vol. I, Section A, p. 1, Cologne, 1960.
6. Stanberry, C. J., T. P. Matson and J. J. Langford, "A Study of Formulation Variables on the Performance of Straight-Chain Alkylbenzene Sulfonates," presented to the Soap and Detergent Association Annual Convention, January 1964.
7. Liddicoet, T. H., and S. A. Olund, JAOCS *40*, 5 (1963).
8. Olson, A. C., Ind. Eng. Chem. *52*, 833 (1960).
9. Weeks, L. E., J. C. Harris and E. L. Brown, JAOCS *31*, 254 (1954).
10. Mayhew, R. L., C. F. Jelinek and A. Stefcik, Soap Chem. Specialties *31*, No. 7, 37, (1955).
11. Spangler, W. G., JAOCS *41*, 300 (1964).
Company Dishwashing Foam Method presented to the ASTM D-12 Subcommittee on Detergents, March, 1959, New York.
12. Schwartz A. M., and J. M. Perry, "Surface Active Agents, Their Chemistry and Technology," Vol. I Interscience, 1949, p. 302.

[Received June 17, 1964—Accepted August 12, 1964]

Straight-Chain Alkylbenzenes: Structure and Performance Property Relations

J. RUBINFELD, E. M. EMERY [1] and H. D. CROSS, III, *Research and Development Department,* Colgate-Palmolive Company, Jersey City, New Jersey

Abstract

An intensive study of the mass spectral characteristics of straight-chain alkylbenzenes has been made in conjunction with their ultimate performance as sulfonates in heavy duty formulations. Two variables of the alkylates, carbon-chain length distribution (which fixes the mean mol wt) and phenyl position on the chain, have been successfully related to the observed dishwashing performances. Formulas are given which allow accurately predicting this performance criteria. The important role of phenyl position is illustrated by a detailed study of each phenyl isomer in the tetradecylbenzene series.

Introduction

THE MOST WIDELY USED SURFACTANT in household detergents for the past 10 years has been polypropylene tetramer branched alkylbenzene sulfonate, commonly known as ABS. Since World War II, the usage of ABS in the U.S. has grown to approx 560 million lb/year. Concurrent with increased use of ABS detergents, our laboratories investigated several hundred commercial polypropylene derived alkylates and were able to correlate performance characteristics with the mass spectrometric analyses.

Fundamentally this correlation depended on the observed molar distribution and also on a branching parameter, both derived from the mass spectral analysis of the alkylate prior to sulfonation. The degree of

---

[1] Colgate-Palmolive Research Center, New Brunswick, N.J.

TABLE I

Alkylate		Mean mol wt	2-Phenyl content (%)	Plates washed: $\frac{LAS}{ABS}$	
				50 ppm	150 ppm
1.	3625	242	34	.47	.76
2.	3362	256	32	.68	.83
3.	3420	257	34	.76	.83
4.	3211	263	30	.75	.84
5.	3136	273	30	.62	.66
6.	3139	285	28	.62	.55

correlation can be exemplified by the fact that the mass spectral analysis has been employed for over five years for pre-screening polypropylene alkylates, with remarkable accuracy. It is our purpose here only to note that this part of our research efforts greatly assisted the detailed work to be described today and will itself form a separate communication for publication.

The advent of the importance of biodegradability dramatically shifted the emphasis from ABS to Linear Alkylate Sulfonates (LAS). The primary objective of our work was to develop an alkylate structure which would meet three major requirements. First, performance must at least equal that of propylene based ABS. Second, the economics must be in the same range. Third, it must be biodegradable. Our main concern in this paper will be the first requirement; that of optimization of the LAS to equal the performance of the ABS to be replaced. Because of the economics, our work was devoted principally to commercially-feasible carbon-chain and phenyl position isomer mixtures. With the initial success with the ABS type materials, our work on LAS seemingly should have been much simpler and straight-forward. Our first efforts in this area began ca. four years ago and resulted in a 90% correlation of the mass spectral analyses to the performance properties of the linear alkylates of that time. The technique employed molar distribution once again and phenyl position analysis. This latter parameter was used to measure the extent of branching and in certain cases the amount of ABS type alkylate present. It is particularly noteworthy that this work was all performed long before the great social and political clamor for biodegradable (e.g. LAS) materials. Indeed, it was recognized as early as 1955 by our laboratories (1) that factors affecting performance of linear alkylbenzenes included phenyl position and chain length.

With the newer and much more linear chained materials going into LAS, these same two parameters derived from the mass spectral analysis have been greatly refined in predicting performance characteristics.

Mass Spectral Analysis

Since the correlations to be described today are based on mass spectral analysis of the starting alkylbenzenes, it is imperative to rapidly summarize this aspect of the work.

The derivation of molar distribution in our laboratories is not markedly different from those methods already published (2,3). While our results do show certain inter-laboratory discrepancies at times, they have been most meaningful in these correlative efforts. The application of either published method would also yield the same correlative degree.

Phenyl position analysis, the second mode of characterizing alkylates in our studies, is by no means unique. That this analysis can be satisfactorily performed by mass spectrometry may be unusual, however. Let us briefly describe this method of computation. The characteristic fragmentations of pure C_{12} linear alkylbenzenes will serve as an example:

Intensity at:	Position of phenyl on C_{12} chain:					
	1-	2-	3-	4-	5-	6-
mass 91	78	12	100	100	100	100
92	100	1	9	9	9	9
105	12	100	8	9	11	13
119	6	1	61	3	3	3
133	7	..	3	37	2	2
147	1	..	2	3	24	..
161	..	..	2	2	2	19

It is readily apparent from this format that the underlined data forms the principal diagonal of a 6 x 6 matrix array. By inverting and applying appropriate sensitivity data, it is a straight-forward matter to solve C_{12} alkylbenzene mixtures for these six isomers.

That this same matrix can be employed for determining the one-through-six phenyl contents for shorter and longer chains that the C_{12} would alone require more time than we have for our purpose here today. We will, however, describe typical results for several other chain lengths, both for individual isomers and for known mixtures.

Alkyl chain	Compounds(s)	Calc. position of phenyl on chain:					
		1-	2-	3-	4-	5-	6-
8	1-phenyloctane	99.96	0	0	0	0	0.04
16	1-phenyl-hexadecane	98.96	0.70	0	0	0	0.33
10	2-phenyl-decane	0.80	98.46	0.25	0.04	0.45	0
20	3-phenyl-eicosane	0.62	0.45	98.93	0	0	0
12	HF-isomers	0	21.4	18.7	19.1	21.8	19.1
12	$AlCl_3$-isomers	0	37.7	17.5	15.0	15.7	12.3
16	$AlCl_3$-isomers	0	36.8	20.7	14.5	15.7	12.3
18	HF-isomers	0	16.5	18.2	20.0	23.0	22.3

Without discussing this table at length, it is important to comment on two significant points. First, for authentic samples of individual isomers, the calculated position commonly runs 98% or better. Second, distributions found for specific olefin-benzene-catalyst reaction products are indeed indicative of the one-through-six isomer distribution found by either fractionation cuts or V.P.C. analyses.

One almost invariably asks the question, "What happens to the 7-,8- and 9-isomer content of a C_{18} isomeric mixture?" In general, these isomers do contribute a very small amt to the calculated one-through-six isomers. However, it is readily apparent, on re-examination of the original 6 x 6 array that the really significant peaks produced by these particular isomers are not included in the matrix. For instance, the 7-phenyl C_{18} isomer shows its strongest fragment ions at 91, 175 and 245—none of which are involved in our system. Thus, the calculation of one-through-six isomers should and does agree closely with their corresponding one-through-six isomeric distribution found by other techniques. We are aware of certain branching and contributory limitations, not unlike those found in V.P.C. and other methods of isomer

TABLE II

Alkylate		Mean mol wt	2-Phenyl content (%)	Plates washed: $\frac{LAS}{ABS}$	
				50 ppm	150 ppm
7.	3186	247	23	.68	.85
8.	3427	256	19	.97	1.08
9.	3586	256	26	.84	.93
10.	3209	257	26	.92	.92
11.	3133	265	25	.82	.78
12.	3156	278	18	.63	.68

determination, but need not pursue them in this discussion.

Evaluation Techniques

As cited earlier, the mass spectral data was determined on the original alkylbenzenes. All evaluation data has been generated using the corresponding alkylbenzene sulfonate as the sole active organic ingredient. The typical heavy duty detergent formulation utilizing either ABS or LAS consisted of 20–25% active ingredient, 35–40% sodium tripolyphosphate, 5–10% sodium orthosilicate, 25–30% sodium sulfate and 5–10% moisture. The foam stability test used was a designed Practical Dishwashing Procedure described in an earlier publication from our research laboratories (4). In this test, all products are examined at 0.15% concn, at 115F and at 50 and 150 ppm hardnesses, employing a hydrogenated vegetable oil type of soil. Under such test conditions the standard ABS washes 20 plates at each hardness. (A total difference of 1 plate is significant at the 95% confidence level. A pooled error variance from 100 sets of duplicate results gave a standard error of ±0.55 plates.) This dishwashing test, along with the additional performance parameters of simulated dishwashing and sebum foam tests, have found great applicability in our laboratories because of the close correspondence to actual laundry performance as regards foam stability.

The standard ABS employed in these studies was a branched "tridecylbenzene" sulfonate derived from essentially C_{11} through C_{16} carbon-chained alkylbenzenes bimodal at C_{12} and C_{15}. All alkylates were sulfonated using standard oleum batch sulfonation. The neutralized LAS and ABS slurries were roll-dried to give a dried sulfonate of ca. 90% active ingredient.

Discussion and Results

1. Work with Mixed Chains

A. Foam Stability Studies

Our earliest studies included numerous linear alkylates having a 2–4 carbon range in the alkyl chains, with some averaging as low as C_9 and as high as C_{18}. The failure of these latter materials to perform in heavy duty formulations surprised no one. They did serve as the extreme boundaries, however.

The first attempts to define alkylate composition related performance to mol wt range. A series of alkylates made by $AlCl_3$-type catalysts suggested that the preferred mol wt was 252–266. This is illustrated in Table I. We have chosen to define all alkylates with a 2-phenyl content of 28% and above to have been made by an $AlCl_3$-type equilibrium catalyst.

Two facts became immediately evident. First, all the alkylates gave substantially poorer performances than the standard tridecylbenzene sulfonate. Second, the one low and two higher mol wt alkylates have significantly poorer performances than the intermediate mol wt compounds. It is of interest to note that a standard branched chain material in use today, tridecylbenzene, has a mean mol wt approximating 264 and that the linear alkylate series with this mol wt approximates the upper limit of the satisfactory performers described thus far.

Our attention was then directed to alkylates made by other methods than $AlCl_3$-equilibrium catalysis, e.g., HF or modified $AlCl_3$ recycle methods. An alkylate with below 28% 2-phenyl was arbitrarily defined as being made by these other methods. As can be noted from Table II, the preferred mol wt range again centered around the 252–266 area.

TABLE III

Alkylate	Mean mol wt	2-Phenyl content (%)	Alkyl distribution			Plates washed: $\frac{LAS}{ABS}$	
			C_{12}	C_{13}	C_{14}	50 ppm	150 ppm
13. 3632	257	32	31	46	19	.74	.84
14. 3576	257	31	39	31	27	.62	.78
15. 3125	264	32	21	29	30	.55	.70
4. 3211	263	30	20	42	30	.75	.84

Thus we arrived at the same preferred area of mol wt 252–266 for alkylates made by both aluminum chloride or hydrogen fluoride catalyzed reactions. The contribution of chain length and of phenyl position becomes evident if we combine portions from Tables I and II with additional mass spectral and performance data. This is illustrated in Table III.

These pairs illustrate the influence of chain contributions, being essentially independent of phenyl position. In particular, the last pair show that the redistribution of C_{13} content into C_{11} and C_{15} homologs materially lowers the performance.

Table IV, on the other hand, is composed of essentially identical alkyl chain distributions, thereby effectively making the sole variable the phenyl position. The specific alkylate pair, 18 and 8, were known to differ only in the mode of catalysis. The improvements in performance found in this table must be attributable to the effects of phenyl position alone.

Outside the range of optimum (mol wt 252–266), where substantial quantities of C_{11} or C_{15} are present in mixed chain alkylates, the contribution of phenyl position is diminished but still present. The interaction of chain length and phenyl position effects undoubtedly produce this apparent diminution. It would be erroneous to assume that in higher or lower mol wt compounds the phenyl position plays no role. In the pure tetradecylbenzene series, as will be demonstrated later, the effect is very pronounced.

Once having established the preferred mol wt area of 252–266, many types of carbon-chain distributions as well as phenyl position isomer combinations were studied within this narrow range. These studies led us to a direct relationship between foam stability characteristics and the amt of 5- and 6-phenyl isomers present. Consider the following series of 12 alkylates illustrated in Table V.

Particular note should be made that Table V was composed of alkylates having 90% or more in the C_{12} through C_{14} chains. The correlation is not restricted to the 90% level, however. It was found that even when the summation of the 12 through 14 chains fell to 50%, one could still accurately predict the performance. This was achieved by employing the same constants already used in calculating performances in Table V, and incorporating an additional deficiency term for the decreased amt of C_{12}–C_{14} chains. Results obtained for these lower C_{12}–C_{14} alkylates are illustrated in Table VI.

TABLE IV

Alkylate	Mean mol wt	2-Phenyl content (%)	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	Plates washed: $\frac{LAS}{ABS}$	
								50 ppm	150 ppm
16. 3160	255.8	34	9.0	32.8	35.7	20.5	1.3	.78	.76
17. 3305	255.6	25	7.4	34.0	32.7	24.5		.90	1.08
18. 3287	256.7	34	4.5	33.9	43.0	15.7	2.3	.71	.76
8. 3427	256.0	19	4.8	34.5	42.8	16.0	1.2	.97	1.08
2. 3362	256.0	32	4.1	31.7	48.2	14.8	.3	.68	.83
10. 3209	256.7	26	.3	33.8	50.2	14.4	.6	.92	.92

It can be seen that, to a close approximation, the analytical data can be used to predict the observed performance. The real import of these relationships lies in the fact that one can screen the linear alkylate raw material and very rapidly and quite accurately predict its ultimate performance as a sulfonate. The greatest deviation in prediction to date has been 2 plates, with most results within 1 plate.

The data thus far has been based on diverse commercial alkylates. A pair of synthetic blends were also studied. The major component in each was an $AlCl_3$-type alkylate, with the minor component being pure tetradecylbenzenes derived from each of the two classes of catalysis already described. The phenyl position plays the same crucial role in these mixed compounds. The results are illustrated in Table VII. It can be seen that blend 2 has superior performance as predicted from all of our earlier observations.

B. Detergency and Biodegradability

Studies in our laboratories have shown the low 2-phenyl mixtures to be better detergents than the high 2-phenyl mixtures in the mol wt range of 252–266. This will be reported more comprehensively in a future publication (5).

Another area of research also reports (6) that mixed chain alkylates with both high and low 2-phenyl contents (e.g. 8 and 18) degrade essentially the same.

2. Work with Pure Isomers

A. Foam Stability Studies

Our results on pure phenyl isomers in the tetradecylbenzene series show that the foam stability of the sulfonates is increased as the phenyl group is moved down the chain from the one to the six position. We have used two dishwashing foam tests as well as the sebum foam test which have been recently published (4) and which show good correlation to practical laundry performance. The results are summarized in Tables VIII and IX.

It will be noted that the same general trend is evident using both dishwashing tests. The 5-, 6-, 7-phenyl isomers are the best performers. The break is sharp in both dishwashing series at 5-phenyl. The unusually low value for 7-phenyl (Practical—150 ppm) is being rechecked. At 50 ppm, an increase in performance of approx 55% was found in going from the 2-phenyl to the 7-phenyl isomer. Similarly, at 150 ppm, one of 20% was found for 2- through 6-phenyl. Thus we see that the influence of phenyl position on performance, originally observed and evaluated in the mixed isomers and mixed chains, has been confirmed with the pure isomers of the C_{14} chain length. The poor performance of 1-phenyl tetradecane is due to its extreme insolubility. It is not included in the

TABLE V

Alkylate	Mean mol wt	% C_{12}–C_{14}	5 + 6 Phenyl content (%)	Plates washed: $\frac{LAS}{ABS}$			
				50 ppm		150 ppm	
				Known	Calc [1]	Known	Calc [2]
8. 3427	256.0	93	39.7	.97	.92	1.08	1.01
9. 3586	255.6	93	38.2	.84	.89	.93	.98
10. 3209	256.7	98	37.1	.92	.86	.92	.95
14. 3576	257.3	97	34.3	.62	.80	.78	.87
4. 3211	262.5	92	34.2	.75	.79	.84	.87
16. 3160	255.8	90	32.4	.78	.75	.76	.83
2. 3362	256.0	95	31.9	.68	.74	.83	.81
13. 3632	257.0	96	31.6	.74	.73	.84	.81
19. 3423	257.0	96	31.5	.70	.73	.76	.80
3. 3420	257.0	99	30.6	.76	.71	.83	.78
20. 3626	256.9	97	30.3	.71	.68	.74	.75
18. 3287	256.7	93	29.1	.71	.68	.76	.74

[1] $2.32 \times (5 + 6\%) \times 10^{-2}$.
[2] $2.55 \times (5 + 6\%) \times 10^{-2}$.

TABLE VI

Alkylate	Mean mol wt	% C_{12}–C_{14}	5 + 6 Phenyl content (%)	Plates washed: $\frac{LAS}{ABS}$			
				50 ppm		150 ppm	
				Known	Calc [1]	Known	Calc [2]
12. 3156	277.7	53	44.1	.63	.60	.68	.66
7. 3186	246.9	71	39.5	.68	.73	.85	.80
21. 3134	269.8	62	38.6	.63	.62	.63	.67
5. 3136	273.1	69	34.3	.62	.61	.66	.67
22. 3255	253.1	85	34.2	.79	.75	.78	.82
23. 3429	267.0	78	32.3	.66	.65	.70	.71
15. 3125	264.2	73	32.1	.55	.60	.70	.66
24. 3309	262.1	82	26.6	.58	.60	.70	.67

[1] $2.32 \times (5 + 6\%) \times 10^{-2} \times (C_{12}\text{–}C_{14}\%)/90$.
[2] $2.55 \times (5 + 6\%) \times 10^{-2} \times (C_{12}\text{–}C_{14}\%)/90$.

TABLE VII

Alkylate	Mol wt	C_{12}–C_{13}–C_{14}	Plates washed: $\frac{LAS}{ABS}$	
			50 ppm	150 ppm
* Blend 1	259	31–36–31	.73	.83
** Blend 2	259	31–36–31	.81	.90

*1 85% 3. 3420 and 15% 25. 3545 (C-14—$AlCl_3$).
**2 85% 3. 3420 and 15% 26. 3546 (C-14—HF).

TABLE VIII

Alkylate-tetradecane	Practical dishwashing Plates washed: $\frac{LAS}{ABS}$		Simulated dishwashing Plates washed: $\frac{LAS}{ABS}$	
	50 ppm	150 ppm	50 ppm	150 ppm
1-phenyl	.33	0	(not run)	
2-phenyl	.65	.78	.63	.88
3-phenyl	.68	.78	.63	.92
4-phenyl	.70	.78	.79	.96
5-phenyl	.90	.93	.92	1.08
6-phenyl	1.15	.90	1.08	1.08
7-phenyl	1.00	.80	1.00	1.08

TABLE IX

Sebum Foam—150 ppm
(Foam heights in inches)

Mg sebum soil added	Std ABS	2-Phenyl	3-Phenyl	4-Phenyl	5-Phenyl	6-Phenyl
Initial—0 mg	1¼	1	1	1¼	1¼	1¼
200 mg	1⅛	..	½	1	1⅛	1⅛
300 mg	1⅛	..	..	¾	1⅛	1⅛
400 mg	1⅛	..	..	..	1⅛	1⅛
500 mg	1	..	..	..	1	1
600 mg	⅞	..	..	..	..	⅜
700 mg			..			..

TABLE X

Detergency—Average Rd Reflectance Values

U.S. Testing	1-Phenyl	2-Phenyl	6-Phenyl	7-Phenyl	Std ABS
50 ppm	30.2	32.8	34.1	34.5	30.3
150 ppm	31.7	32.9	35.1	36.4	36.6
200 ppm	28.6	32.8	35.8	36.4	36.6
Test Fabrics					
50 ppm	43.2	44.1	45.8	47.1	42.8
150 ppm	44.1	44.3	45.8	47.6	44.3
200 ppm	38.4	44.4	47.0	47.8	44.1

sebum foam test that follows because it had no initial foam.

The 2- and 3-phenyl compounds had a lower initial foam height which collapsed quickly under the initial sebum soil additions. The 4-phenyl had an intermediate foam pattern whereas the 5- and 6-phenyl compounds were equal to standard at 500 mg soil load and the whole foam pattern closely resembled that the standard. For a detailed analysis of the sebum soil and simulated dishwashing tests, refer to the work of W. Spangler (4) of our laboratories.

B. Detergency Studies

Detergency was measured as the increase in reflectance after washing U.S. Testing and Test Fabric soiled cloths in a Terg-O-Tometer at 0.15% concn, 6 swatches/liter, 10 min at 120F and 100 rpm. There was significant increase (1.2 units is significant at 95% confidence level) in detergency for the 6- and 7-phenyl tetradecylbenzenes as compared to the 1- and 2-phenyl tetradecylbenzenes. This is illustrated in Table X.

We have established that the internal 5- and 6-phenyl isomers are better foamers in mixed chain alkylates than the 1-,2-,3- and 4-isomers. We have shown that the performance of tridecylbenzene sulfonate (ABS) can be matched in detergency and foam performance by optimizing linear alkylate structure. This structure should be in the mol wt area of 252–266 with 90% of the carbon chains being C_{12}, C_{13} and C_{14} and with less than 10% C_{11} or C_{15} and should have approx 40% 5- and 6-phenyl content and 20% 2-phenyl content.

We have also shown that in the pure tetradecylbenzene series of isomers, those with the phenyl centrally located on the chain are ca. 50–80% better foam performers than the 2-isomer. Similarly, the detergency using standard soiled cloth is also better for the internal isomer.

ACKNOWLEDGMENT

Commercial samples contributed by: Allied Chemical, Atlantic Refining, Continental Oil, Gulf Oil, Monsanto, Oronite, Phillips Petroleum, Shell Oil and Union Carbide's Olefin Division. Pure tetradecylbenzene isomers supplied by the Olefin Div. of Union Carbide. Personal acknowledgments to W. Spangler, L. Levinsky, V. J. Richter and the staff of the Household Products Division; W. Casazza and S. Babulak and the overall cooperation of the Analytical Sec.

REFERENCES

1. Gray, F. W., J. F. Gerecht and I. J. Krems, J. Org. Chem. *20*, 520 (1955).
2. Brown, R. A., D. J. Skahan, V. A. Cirillo and F. W. Melpolder, Anal. Chem. *31*, 1531 (1959).
3. Boyer, E. W., M. C. Hamming and H. T. Ford, *Ibid. 35*, 1168 (1963).
4. Spangler, W. G., JAOCS *41*, 300 (1964).
5. Trowbridge, J. R., and J. Rubinfeld, "A Comparison of Two Straight-Chain Sodium Alkylbenzene Sulfonates in a Natural Soil Detergency Test," presented at 4th International Congress on Surface Active Substances, Brussels, Belgium, 1964.
6. Data on biodegradation was supplied by the Microbiology Section of Colgate-Palmolive Co. For published results showing this same effect, see: Sweeney, W. A., Soap Chem. Spec. *40*, No. 3, 45 (1964).

[Received June 17, 1964—Accepted October 15, 1964]

An Evaluation of the River Die-away Technique for Studying Detergent Biodegradability

E. A. SETZKORN, R. L. HUDDLESTON and R. C. ALLRED, Continental Oil Company, Research and Development Department, Ponca City Oklahoma

Abstract

The accuracy and reproducibility of the river die-away test has not been well defined. This information is required to establish the validity of observed differences in degradation behavior.

The present paper presents data on the accuracy and repeatability of the methylene blue analytical procedure using both the standard method and the automated "AutoAnalyzer" version of the methylene blue method.

Data are also presented showing reproducibility of the biodegradation curves obtained by replicate analysis of a single detergent under 1) identical die-away conditions, and 2) different conditions obtained by die-away studies in various river waters.

The effect of detergent mol wt and microbial adaptation to the test substance on the degradation pattern is also discussed.

Introduction

DETERGENT BIODEGRADATION STUDIES have been reported utilizing a variety of biological test systems. Generally, however, these systems may be classified as either static or dynamic. Recent efforts in the development of dynamic systems have been directed toward the development of apparatus and procedures that are simple to maintain and operate in an average laboratory. These dynamic units are operated on the continuous feed principle, designed to simulate conditions in an activated sludge type sewage plant.

The river die-away technique is an example of the static type biological system, and has been extensively used in detergent biodegradation studies. This test have several advantages over other biodegradation test systems. These include the experimental test simplicity and the low solids content of the system which facilitates isolation, or other analytical techniques