March 1, 1949. R. L. SMITH ET AL 2,463,497

WETTING AGENTS

Filed Feb. 23, 1946 4 Sheets-Sheet 1

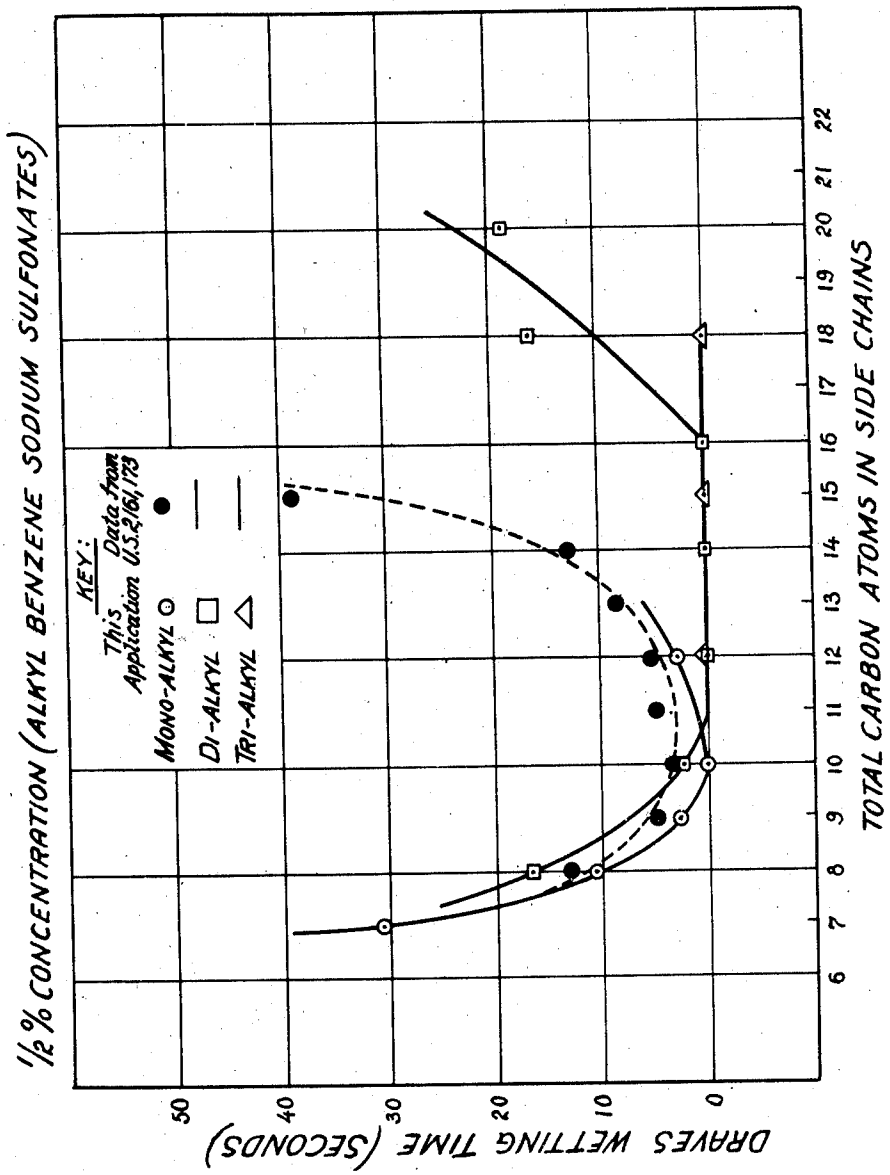


Fig. 1.

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WETTING AGENTS

Filed Feb. 23, 1946 4 Sheets-Sheet 2

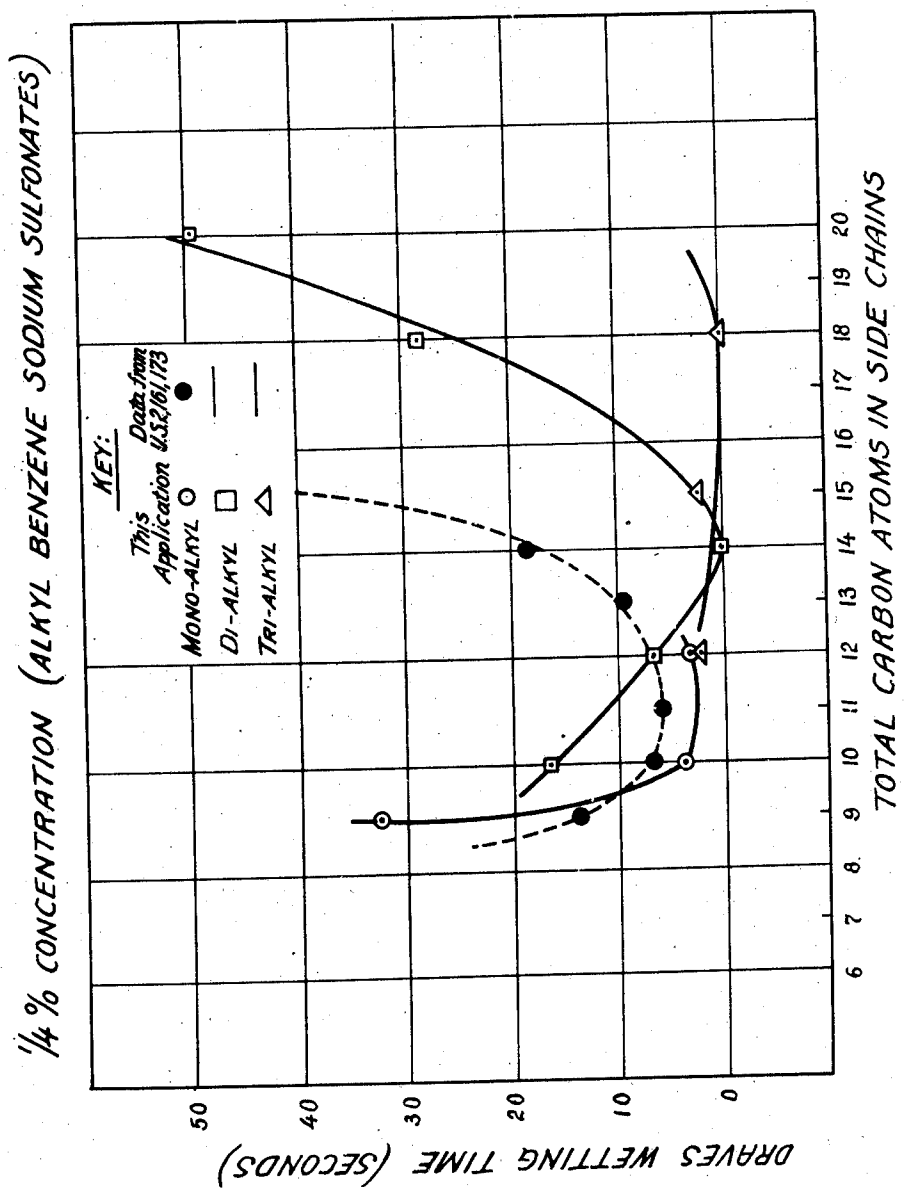


Fig. 2.

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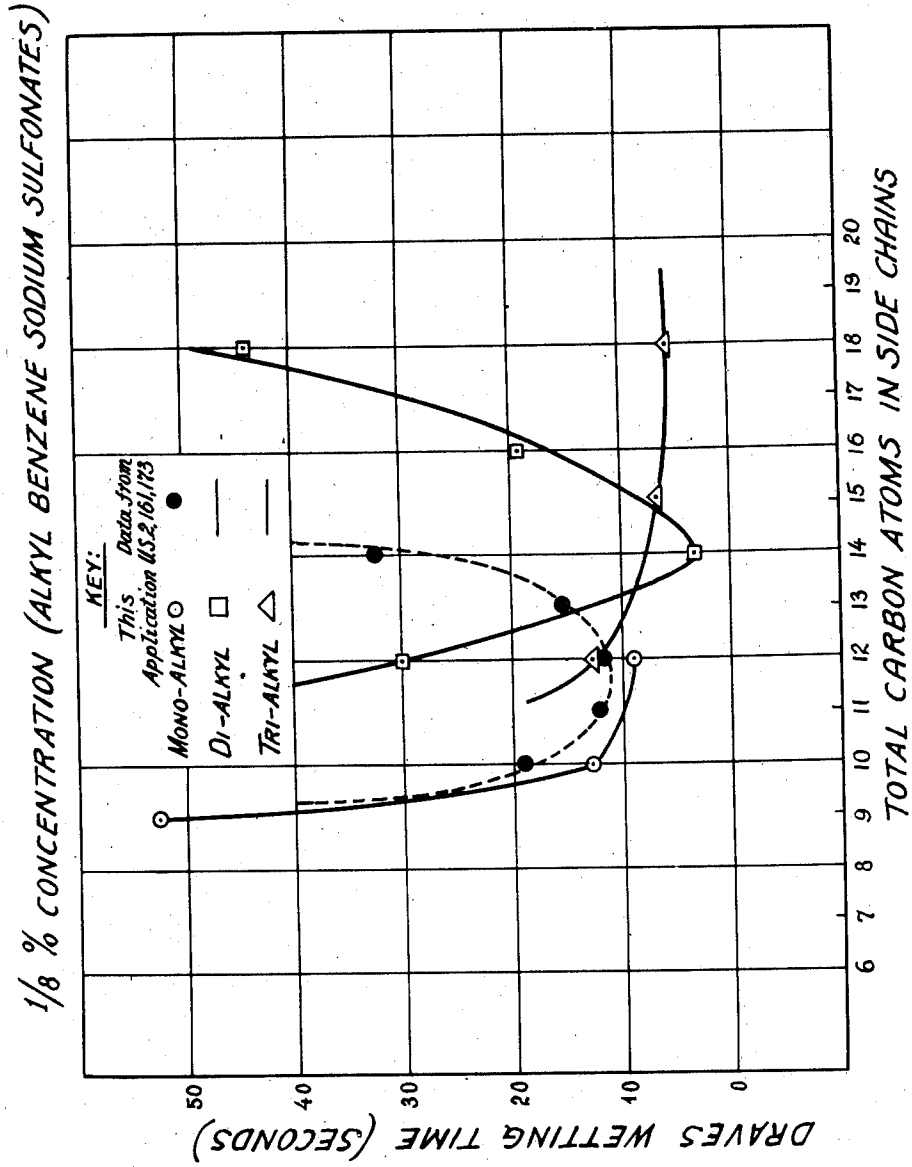
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WETTING AGENTS

Filed Feb. 23, 1946 4 Sheets-Sheet 3

Fig. 3.



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WETTING AGENTS

Filed Feb. 23, 1946 4 Sheets-Sheet 4

Fig. 4.

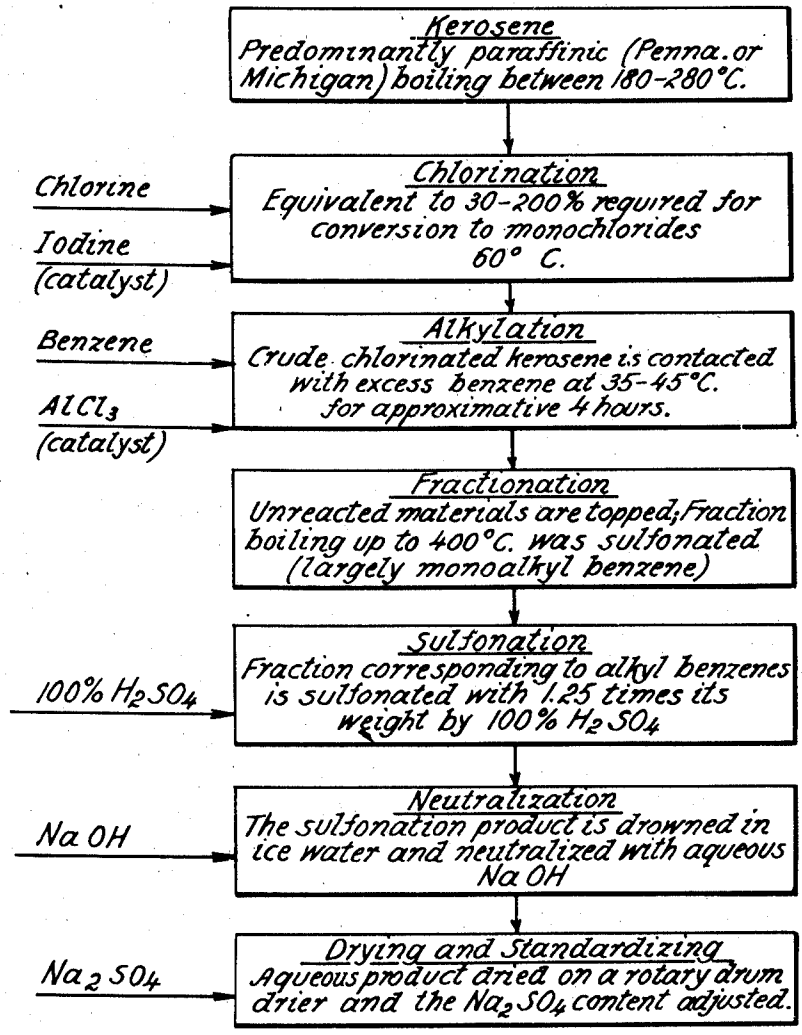
PRODUCTION OF ALKYL-ARYL SULFONATES

$$RH + Cl_2 \xrightarrow{I_2} RCl + HCl$$

$$RCl + C_6H_6 \xrightarrow{AlCl_3} RC_6H_5 + HCl$$

$$RC_6H_5 + H_2SO_4 \longrightarrow RC_6H_4SO_3H$$

$$RC_6H_4SO_3H + NaOH \longrightarrow RC_6H_4SO_3Na + H_2O$$



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UNITED STATES PATENT OFFICE

2,463,497

WETTING AGENTS

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Application February 23, 1946, Serial No. 649,729

5 Claims. (Cl. 260—505)

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The present invention relates to wetting agents and, more particularly, to improved wetting agents providing maximum wetting at lower concentrations than prior art agents.

Although the literature pertaining to wetting agents and detergents is replete with descriptions of various wetting agents such as alkali metal salts of alkylated benzene sulfonic acids, alkylated polynuclear aromatic sulfonic acids and the like, none of the prior art products gives instantaneous wetting at low concentrations of wetting agent when tested by the Draves wetting test.

It has now been discovered that the wetting time in the Draves test can be controlled and reduced to instantaneous at concentrations of 0.5 per cent by weight of wetting agent and less by controlling the number and molecular weight of the alkyl substituents of the aromatic sulfonic acid, the alkali metal salt of which is the preferred form of the wetting agent.

The prior art has established that the monoalkylated benzene sulfonic acids which in the form of their sodium salts are most effective in the Draves wetting test, i. e., have the lowest wetting time, are those having side chains containing 10 to 14 carbon atoms. This is confirmed by the following tabulation of wetting times taken from the patent literature:

	No. of Carbon Atoms in Alkyl Substituents	Wetting Time, sec.		
		.5%	.25%	.125%
Sodium Heptyl benzene sulfonate	7	30.3	300+	--------
Sodium Octyl benzene sulfonate	8	12.7	180+	--------
Sodium Nonyl benzene sulfonate	9	4.6	13.8	188
Sodium Decyl benzene sulfonate	10	3.0	6.8	18.9
Sodium Undecyl benzene sulfonate	11	4.2	6.0	12.0
Sodium Dodecyl benzene sulfonate	12	5.0	6.5	8.9
Sodium Tridecyl benzene sulfonate	13	8.1	9.5	15.2
Sodium Tetradecyl benzene sulfonate	14	12.4	18.6	32.4
Sodium Pentadecyl benzene sulfonate	15	38.6	60.9	91.3
Sodium Hexadecyl benzene sulfonate	16	92.0	235	300+

It will be noted that none of these sodium alkyl benzene sulfonates has a Draves wetting time of

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less than 3 seconds at 0.5 per cent concentration. On the other hand, when the number of alkyl substituents and the total molecular weight of the alkyl substituents are controlled instantaneous wetting in the Draves test can be obtained at concentrations of 0.25 per cent by weight. This enables the operator to use less of the novel wetting agents than of the prior art wetting agents having one or two alkyl substituents of uncontrolled character.

It is an object of the present invention to provide wetting agents comprising alkyl substituted benzene sulfonic acid salts of alkali metals including ammonia in which the total number of carbon atoms in the substituent chains and the number of substituent chains are controlled within critical limits. It is another object of the present invention to provide alkyl substituted polynuclear aromatic sulfonic acid salts of alkali metals including ammonia in which the total number of carbon atoms in the substituent chains and the number of substituent chains are controlled within critical limits. It is a further object of the present invention to provide alkyl substituted polynuclear aromatic sulfonic acid salts of alkali metals including ammonia derived from aromatic petroleum stocks. The present invention also has as an object the provision of means for producing the novel sulfonic acids from aromatic petroleum stocks. Other objects and advantages will become apparent from the following description taken in conjunction with drawings in which:

Figure 1 is a graph illustrating the relation between wetting time as determined by the Draves test and the number of substituent chains and the total number of carbon atoms in the substituent chains for alkyl benzene sodium sulfonates at 0.5 per cent concentration of the salt by weight;

Figure 2 is a graph illustrating the same relation at a concentration of 0.25 per cent by weight alkyl benzene sodium sulfonate;

Figure 3 is a graph illustrating the same relation at a concentration of 0.125 per cent by weight alkyl benzene sodium sulfonate; and

Figure 4 is a flowsheet illustrative of a method for producing the novel wetting agents.

The drawings illustrate in a graphic manner the differences between the prior art alkyl benzene sulfonates and the novel sulfonates in which

the number of substituent groups and the total number of carbon atoms in the substituent groups are controlled. For example, even cursory inspection of Figure 1 reveals the fact that at 0.5 per cent concentration only one alkyl benzene sodium sulfonate having one alkyl chain has a wetting time in the Draves test approaching instantaneous. On the other hand, those alkyl benzene sodium sulfonates having two substituent alkyl groups and having 11 to 16 total carbon atoms in the substituent groups give instantaneous wetting in the Draves test. Similarly, those alkyl benzene sodium sulfonates having 3 substituent groups having a total of 12 to 18 carbon atoms in the substituent groups likewise give instantaneous wetting time in the Draves test. In other words, while instantaneous wetting is obtainable in the one substituent group with one sulfonate only, decyl benzene sodium sulfonate, it is obtainable with 6 sulfonates in the two substituent group and with 7 in the three substituent group. (Any discrepancy between the foregoing statement and the data given in the previous tabulation is due to the different sources of the data. Because of the nature of the material and the method of testing, the variations are reasonable.)

Figure 2 illustrates a further distinction between the novel alkyl aromatic sodium sulfonates and the prior art sulfonate wetting agents. Whereas at 0.25 per cent concentration by weight none of the mono-substituent benzene sodium sulfonates give instantaneous wetting time in the Draves test, of the novel wetting agents, one di-substituted and three tri-substituted benzene sodium sulfonates give instantaneous wetting in the Draves test.

Figure 3 illustrates another distinction between the novel wetting agents and the prior art wetting agents. If a wetting time of 10 seconds in the Draves test be taken as the dividing line between satisfactory and unsatisfactory wetting agents, Figure 3 establishes that at 0.125 per cent concentration by weight polyalkylated benzene sodium sulfonates having between 13 and 18 total substituent carbon atoms are satisfactory wetting agents, whereas the mono-substituted sulfonates are limited to those having 11 and 12 carbon atoms. In other words, great flexibility in manufacture is the result of controlling the number of substituent groups and the total number of substituent carbon atoms. It will also be observed that as the number of substituent groups is increased the total number of substituent carbon atoms may be increased and instantaneous wetting time retained. In this connection it will be pointed out that at a concentration of 0.125 per cent by weight two mono-substituted alkyl benzene sodium sulfonates having 11 and 12 total carbon atoms in the alkyl group are satisfactory wetting agents and three di-substituted alkyl benzene sodium sulfonates having 13 to 15 carbon atoms in the substituent chains are satisfactory wetting agents whereas 8 tri-substituted benzene sodium sulfonates having a total of 13 to 20 carbon atoms in the substituent chains are satisfactory wetting agents as determined by the Draves test. (A satisfactory wetting agent is one which has a wetting time of 10 seconds or less in the Draves test.) This provides great flexibility in the preparation of the alkyl substituted benzene sulfonic acids from which the alkali salts are obtained since the more readily available hydrocarbons of from 4 to 8 carbon atoms may be used whereas in the prior art the less readily available higher molecular weight hydrocarbons had to be employed to produce the prior art wetting agents with their inherent deficiencies as compared to the novel wetting agents.

A similar relation exists between the mono-alkylated and polyalkylated polynuclear aromatic alkali metal sulfonates as wetting agents. This is most easily illustrated by the naphthalene sodium sulfonates in the following tabulation:

TABLE I

Hydrocarbon Sulfonated	No. of Substituent Groups	Total Carbon Atoms Substituents	[1] Wetting Time in Seconds at—				
			2% by wt.	1% by wt.	0.5% by wt.	0.25% by wt.	0.125% by wt.
Naphthalene			300+				
Trimethyl Naphthalene	3	3	300+				
Amyl Naphthalene	1	5	5.8	16.9	119	300+	
Monoisopropyl [2] Trimethyl Naphthalene	4	6			105	300+	
Monobutyl [3] Trimethyl Naphthalene	4	7			21	76	300+
Monoamyl [4] Trimethyl Naphthalene	4	8			16	300+	
Diisopropyl [4] Trimethyl Naphthalene	5	9			13.1	198	300+
Diamyl Naphthalene	2	10			1	2.9	300+
Dibutyl [6] Trimethyl Naphthalene	5	11			Inst.	4.8	20
Mono- and diamyl [7] Trimethyl Naphthalene	5	13			3.4	14	77
Tri- and Tetra-Amyl [8] Trimethyl Naphthalene	7	23			49	95	265
Alkylated [9] Trimethyl Naphthalene					4.9	23	158
Alkylated [10] Trimethyl Naphthalene					1.5	5.5	19

[1] Draves Wetting Test.
[2] Alkylate (B. R. 513-603° F.) from aromatic petroleum stock alkylated with refinery C_3 fraction containing about 40 per cent propylene.
[3] Alkylate (B. R. 590-648° F.) from aromatic petroleum stock alkylated with diisobutylene.
[4] Alkylate (B. R. 606-653° F.) from aromatic petroleum stock alkylated with mixed amylenes.
[5] Alkylate (B. R. 603-644° F.) from aromatic petroleum stock alkylated with refinery C_3 fraction containing about 40 per cent propylene.
[6] Alkylate (B. R. 648-698° F.) from aromatic petroleum stock alkylated with diisobutylene.
[7] Alkylate (B. R. 619-766° F.) from aromatic petroleum stock alkylated with mixed amylenes to an average of 1.7 amyl groups.
[8] Residue of aromatic petroleum stock boiling above 766° F. alkylated with mixed amylenes to about 3.7 amyl groups.
[9] Alkylate (B. R. 617-676° F.) from aromatic petroleum stock alkylated with thermal gasoline B. R. 104-347° F.
[10] Alkylate (B. R. 676-766° F.) from aromatic petroleum stock alkylated with thermal gasoline B. R. 104-347° F.

The aromatic petroleum stock boiling above 513° F. has as a major alkylatable and sulfonatable component trimethyl naphthalene.

The study of the data presented in Table II provides the basis for a generalization predicated

on the hypothesis that the ratio between the calculated molecular weight of all of the alkyl substituent groups of a sodium salt of an aromatic sulfonic acid wetting agent, "A," and the calculated molecular weight of the residual portion of the salt, "B," is a means of distinguishing satisfactory wetting agents (as defined hereinbefore) from unsatisfactory wetting agents of this class. Thus, for monoheptyl benzene sodium sulfonate, $C_7H_{15}C_6H_4SO_3Na$, A is C_7H_{15} having a molecular weight of 99 and B is $C_6H_4SO_3Na$ having a molecular weight of 179. Then

$$\frac{A}{B} \text{ is } \frac{99}{179} \text{ or } 0.552$$

The ratio

$$\frac{A}{B}$$

for dibutyl benzene sodium sulfonate

$$(C_4H_9)_2C_6H_3SO_3Na$$

is calculated in a similar manner. A is $(C_4H_9)_2$ or 114 and B in $C_6H_3SO_3Na$ or 178. Consequently,

$$\frac{A}{B} \text{ is } \frac{114}{178} \text{ or } 0.640$$

This value

$$\frac{A}{B}$$

for triamyl benzene sodium sulfonate

$$(C_5H_{11})_3C_6H_2SO_3Na$$

is calculated from A or $(C_5H_{11})_3$ or 213 and B or $C_6H_2SO_3Na$ or 177 as

$$\frac{A}{B}=\frac{213}{177} \text{ or } 1.202$$

Similarly,

$$\frac{A}{B}$$

for tri- and tetramyltrimethyl naphthalene sodium sulfonate, $(C_5H_{11})_{3.7}(CH_3)_3C_{10}HSO_3Na$ is calculated from A or $(C_5H_{11})_{3.7}(CH_3)_3$ or 308 and B or $C_{10}HSO_3Na$ or 224 to be

$$\frac{308}{224} \text{ or } 1.377$$

A study of the data provided hereinbefore and in Table II following provides basis for this generalization that when the ratio of the calculated molecular weight of the alkyl substituents (A) to the calculated molecular weight of the residue of the sodium salt of the sulfonic acid (B) is between about 0.65 and about 1.06 for monoalkylated acids, between about 0.7 and about 1.46 for dialkylated acids and between about 0.96 and about 2.15 for tri- and higher alkylated acids, a satisfactory wetting agent at 0.5 per cent concentration by weight is obtained. Furthermore, for polynuclear aromatic alkali metal sulfonates a satisfactory wetting agent is obtained when the ratio A:B is equal to about 0.71 to about 0.84. Accordingly, the novel wetting agents may be defined as poly-alkylated mono- and polynuclear aromatic alkali metal sulfonates in which the ratio of the calculated molecular weight of the alkyl substituents to the calculated molecular weight of the residue of the sodium salt is between about 0.73 to about 2.2 and there are 2 or more alkyl substituents having a total of at least eight carbon atoms.

TABLE II

Alkyl aromatic sodium sulfonates

Na salt of sulfonic acid of	No. of carbon atoms in substituent group	A / B	Wetting time in seconds at 0.5% concentration by wt. of sodium salt of the sulfonic acid
ONE SUBSTITUENT GROUP			
Heptyl benzene	7	0.552	30.3
Octyl benzene	8	0.631	12.7
Nonyl benzene	9	0.710	4.6
Decyl benzene	10	0.787	3.0
Undecyl benzene	11	0.865	4.2
Dodecyl benzene	12	0.944	5.0
Tridecyl benzene	13	1.023	8.1
Tetradecyl benzene	14	1.100	12.4
Pentadecyl benzene	15	1.179	38.6
Hexadecyl benzene	16	1.256	92.0
Amyl naphthalene	5	0.31	119.0
TWO SUBSTITUENT GROUPS			
Dibutyl benzene	8	0.640	16.4
Diamyl benzene	10	0.797	2.2
Diamyl naphthalene	10	0.623	(1)
Dihexyl benzene	12	0.955	(1)
Diheptyl benzene	14	1.112	(1)
Dioctyl benzene	16	1.270	(1)
Dinonyl benzene	18	1.429	16.4
Didecyl benzene	20	1.583	18.7
THREE SUBSTITUENT GROUPS			
Trimethyl naphthalene	3	0.199	300+
Triisopropyl benzene	9	0.728	300+
Tri-t-butyl benzene	12	0.965	(1)
Triamyl benzene	15	1.202	(1)
Trihexyl benzene	18	1.440	(1)
Trioctyl benzene	24	1.914	5.9
FOUR SUBSTITUENT GROUPS			
Monoisopropyl trimethyl naphthalene	6	0.390	105.0
Monobutyl trimethyl naphthalene	7	0.451	21.0
Monoamyl trimethyl naphthalene	8	0.513	16.0
Tetraisopropyl benzene	12	0.977	17
Tetrabutyl benzene	16	1.295	6.2
Tetraamyl benzene	20	1.60	9.2
FIVE SUBSTITUENT GROUPS			
Diisopropyl trimethyl naphthalene	9	0.552	13.1
Mono- and diamyl trimethyl naphthalene	8.5	0.738	3.4
Dibutyl trimethyl naphthalene	11	0.707	(1)
SIX SUBSTITUENT GROUPS			
Tri- and tetraamyl trimethyl naphthalene	21.5	1.377	49.0

[1] Instantaneous.

The alkyl-aryl sulfonates of the prior art are derivatives of the benzene, naphthalene and diphenyl series or substituted members of the series such as compounds containing nuclear substituents. The alkyl group of the sulfonates is derived from a paraffinic petroleum distillate such as kerosene or a "white oil" fraction. A flow-sheet representative of prior art practice for producing the monoalkyl-aryl sulfonates is provided in Figure 4.

Since the kerosene is chlorinated so that the gain in chlorine content is equivalent to 30 to 200 per cent of that required for monochlorination, there are polychlorides in the chlorination product. Thus, the alkylated product contains such

compounds as diaryl alkanes and dialkyl benzenes. While it is possible to sulfonate the total alkylated product, it is more desirable to distill the alkylated material and sulfonate the distillate.

The effectiveness of the wetting agents is largely dependent upon the balance between the hydrocarbon and inorganic portions of the molecule. By increasing the size of the alkyl group the resulting sulfonate will become more and more effective until a point of maximum effectiveness is reached, after which any increase in the size of the alkyl group will be detrimental. The effective range for sulfonates containing one alkyl group varies from 10 to 16 carbon atoms in the alkyl group. This effect apparently holds true with respect to both wetting and detergent properties. The data supplied in U. S. Patents No. 2,161,173 and No. 2,161,174 verify the foregoing statements.

The effectiveness of a wetting agent or detergent is most readily determined by the "Draves" testing procedure (1937 yearbook of the American Association of Textile Chemists and Colorists). It is the time expressed in seconds required for a 5 gram skein of 40/2 unboiled cotton yarn with a 1.5 grams hook attached to sink when held totally immersed in the solution by means of a thread attached to a 20 grams weight. The wetting time is the elapsed time between the moment at which the skein and weight are dropped into the solution and the first visible indication of any relaxation of the tension of the thread connecting the skein and the weight.

The novel alkyl-aryl sulfonates which are described in this application may be prepared in any suitable manner and were prepared in a manner similar to that employed in commercial practice. The principal differences in constitution are that these sulfonates have two or more alkyl groups attached to the aromatic ring or rings and that they may be mixtures of mono- di- and trialkylated aryl sulfonates having a controlled total number of substituent carbon atoms, whereas the present commercial products are essentially monoalkyl benzene sulfonates. In the novel alkyl-aryl sulfonates the size and number of alkyl groups attached to the aromatic ring are controlled in order to obtain maximum wetting power with flexibility of manufacture.

In order to prepare the desired alkyl-aryl sulfonates the hydrocarbon chlorides were condensed with the desired aromatic compound in the presence of aluminum trichloride. It will be recognized that in the presence of the aluminum trichloride rearrangements are likely to take place to some extent. The alkylated products were fractionated and fractions or cuts of the distillate that corresponded to the boiling range of known compounds were sulfonated. However, in industrial operation the entire topped alkylate may be sulfonated. The range of effective wetting agents varies from diamyl to didecyl benzene sodium sulfonates, with diheptyl benzene sodium sulfonate being the most effective. It is interesting to note the comparison between the monoalkyl and the dialkyl derivatives. Essentially, the influence of two alkyl groups is to improve the efficiency of the sulfonates and to increase the number of carbon atoms in the alkyl groups required to balance the polar and nonpolar parts of the molecule. For example, diamyl and dihexyl benzene sodium sulfonates are not quite as effective as the monoalkyl derivatives having the same total number of carbon atoms in the substituent group. On the other hand, diheptyl, dioctyl, dinonyl and didecyl benzene sodium sulfonates are far superior to the monoalkyl derivatives having the same total number of carbon atoms in the substituent.

The same general relation holds true for the trialkyl benzene sodium sulfonates. While the data are not as complete as for the dialkyl derivatives, it should be recognized that it is difficult to isolate the higher boiling products in appreciable quantities of assured purity because of the complexity and non-volatility of the molecule. The effective wetting range varies from tributyl benzene sodium sulfonate to trinonyl benzene sodium sulfonate. Triamyl benzene sodium sulfonate appears to represent the most effective wetting agent of this type. It is interesting to note that trioctyl and trinonyl benzene sodium sulfonates have acceptable wetting times of 5.9 seconds at 0.5 per cent concentration for trioctyl benzene sodium sulfonate and 6.1 seconds at 0.5 per cent concentration for trinonyl benzene sodium sulfonate. These values are to be contrasted with the wetting times for tricosyl (23 carbon atoms mono-substituent) benzene sodium sulfonate given in U. S. Patent No. 2,161,173 as 2 hours, 5 minutes at 0.5 per cent, 3 hours at 0.25 per cent and 3 hours and 15 minutes at 0.125 per cent concentration.

The structure of the alkyl groups attached to the aromatic ring influences the wetting power of the sulfonate appreciably. Data relative to dihexyl and diheptyl benzenes in which the alkyl groups are derived from normal paraffins, branched-chain paraffins and alicyclic hydrocarbons are set forth in the following table:

TABLE III

Sodium salt of the sulfonic acid of	Substituent derived from	Wetting time in seconds at a concentration by wt. of—			
		0.5%	0.25%	0.125%	0.0625%
Dihexyl benzene	neohexane	29.6	300+		
Do	n-hexane	(1)	6.9	29.6	
Do	cyclohexane	6.0	33.8	300+	
Diheptyl benzene	n-heptane	(1)	(1)	3.4	12.8
Do	methyl cyclohexane	17.3	148.1	300+	
Do		40.7	300+		

[1] Instantaneous.

Although it has been accepted in the art and has been shown hereinbefore that mono-substituted alkyl-aryl sodium sulfonates having less than 10 carbon atoms in the substituent group are poor wetting agents, these poor agents can be improved to produce satisfactory agents by the

addition of disubstituted aryl sulfonates. Illustrative of this are the combinations set forth in Table IV:

TABLE IV

	Wetting time in seconds at a concentration by wt. of—			
	0.5%	0.25%	0.125%	0.0625%
Heptyl benzene sodium sulfonate (*a*)	30.3	300+		
Diheptyl benzene sodium sulfonate (*b*)	Instantaneous.	Instantaneous.	3.4	12.8
67% *a*+33% *b*	Instantaneous.	17.2	37.0	300+
80% *a*+20% *b*	2.5	25.1	146.1	300+
Heptyl benzene sodium sulfonate (*c*) heptyl=chlorinated gasoline fraction.	12.9	187.5	300+	
Diheptyl benzene sodium sulfonate (*d*) heptyl=chlorinated gasoline fraction.	Instantaneous.	Instantaneous.	6.7	45.3
67% *c*+33% *d*	2.7	19.2	153.8	
50% *c*+50% *d*	Instantaneous.	8.6	51.3	

(*a*) Mid-Continent stock.
(*b*) Mid-Continent stock.
(*c*) Michigan stock.
(*d*) Mixture of Mid-Continent and Coastal stocks.

An application of the principles of the present invention involves the use of gasoline straight run or thermally cracked and illustrated by the following data:

TABLE V

	Wetting time in seconds at a concentration by wt. of—			
	0.5%	0.25%	0.125%	0.0625%
Diheptyl benzene sodium sulfonate heptyl=straight run gasoline (*a*) (85–108° C.)	Instantaneous.	Instantaneous.	6.7	45.3
Diheptyl benzene sodium sulfonate heptyl=straight run gasoline (*b*) (86–105° C.)	Instantaneous.	3.0	15.7	117.1
Diheptyl benzene sodium sulfonate heptyl=straight run gasoline (*c*) (95–100° C.)	Instantaneous.	Instantaneous.	3.4	12.8
Diheptyl benzene sodium sulfonate heptyl=thermal gasoline (*d*) (80–108° C.)	14.6	37.3	102	

(*a*) Mid-Continent stock.
(*b*) Mid-Continent stock.
(*c*) Michigan stock.
(*d*) Mixture of Mid-Continent and Coastal stocks.

While it has been shown hereinbefore that an increase in the number of substituent groups increases the effectiveness of the sulfonic acid among the alkyl benzene sulfonates, there is a definite limit beyond which the wetting power decreases. This can be readily appreciated from the data contained in Table VI:

TABLE VI

	No. of substituent groups	$\frac{A}{B}$	Wetting time in seconds at a concentration by wt. of—		
			0.5%	0.25%	0.125%
Dibutyl benzene (446–473° F.) sodium sulfonate	2	0.637	3.7	64	300+
Tributyl benzene (540–550° F.) sodium sulfonate	3	0.960	(1)	6.5	48
Tetrabutyl benzene (608–662° F.) sodium sulfonate	4	1.29	6.2	34.4	300+
Diamyl benzene sodium sulfonate	2	0.797	2.2		
Triamyl benzene sodium sulfonate	3	1.202	(1)		
Tetraamyl benzene sodium sulfonate	4	1.60	9.2	14.9	35.3
Mono- and diamul trimethyl naphthalene	4+	.738	3.4		
Tri- and tetraamyl trimethyl naphthalene sodium sulfonate	6+	1.377	49.0		

[1] Instantaneous.

Illustrative of the preparation of a few of the alkyl-aryl sodium sulfonates are the following examples:

EXAMPLE I

HEPTYL BENZENE SODIUM SULFONATE

Chlorination

A 3 liter three-necked flask equipped with a stirrer, reflux condenser, thermometer and chlorine gas inlet was charged with 2 liters (1351 grams) of technical normal heptane. Chlorine was introduced into the flask while the temperature was maintained at 60–65° C. until the increase in weight was 125 grams. A 60 watt electric light bulb hung just outside the flask was used for actinic light source. After chlorination the reaction mixture was blown with nitrogen to remove dissolved chlorine and hydrogen chloride. The product was fractionated and a cut boiling between 118° C. and 155° C. was separated as chloroheptanes.

Alkylation

To a 3 liter three-necked flask equipped with a stirrer, reflux condenser, thermometer and separatory funnel, 9 moles (702 grams) of benzene and 0.34 mole (45 grams) of aluminum chloride were charged. Three moles (403 grams) of chloroheptanes were placed in the separatory funnel and added slowly for 1.5 hours while the

contents of the flask were stirred at 50° C. This temperature was maintained an additional 2 hours, stirring continuously. The reaction mixture was cooled and quenched with 400 grams of ice water. The organic layer was separated and dried with calcium chloride. It was finally filtered through a 50:50 Hiflo-Super Filtrol mixture and fractionated. The fraction boiling between 228–234° C. was sulfonated as monoheptyl benzenes and the fraction 312–343° C. was sulfonated as diheptyl benzenes.

Sulfonation

A. *Monoheptyl benzene.*—One hundred milliliters (85 grams) of monoheptyl benzene was charged with 100 milliliters of liquid sulfur dioxide into a Dewar flask equipped with a stirrer and a drain stopcock. Ninety-four grams of 60 per cent oleum in 130 milliliters of liquid sulfur dioxide was used as the sulfonating agent. The sulfonation mixture was quenched with 95 milliliters of water; the temperature rose to 45° C. One hundred milliliters of 91 per cent isopropyl alcohol was added and an acid layer separated. The sulfonation product was neutralized with 67 milliliters of 50 per cent by weight sodium hydroxide solution.

The sulfonate solution was extracted with 5 (150 milliliters) portions of intermediate naphtha. It was dried on a drum dryer. The dry crude sulfonates were dissolved in approximately 1 liter of absolute methanol and heated to reflux temperature. The inorganic salts were removed by filtration and 91 grams of purified sulfonates were recovered from the filtrate after it had been dried. The purified product gave the following wetting tests:

Concentration (per cent)	2	1	½	¼
Wetting time (seconds)	2.6	9.1	30.3	300+

B. *Diheptyl benzene.*—The diheptyl benzene was sulfonated in fashion similar to that described for monoheptyl benzene. The product gave instantaneous wetting at ½ and ¼ per cent concentrations, 3.4 seconds at ⅛ per cent and 12.8 seconds at 1/16 per cent.

EXAMPLE II

Heptyl Benzene Sodium Sulfonates

Chlorination

Michigan straight-run gasoline was fractionated in a fifty-plate column and fractions boiling between 95–100° C. were combined corresponding to the boiling range of normal heptane. One thousand four hundred and thirteen grams of the n-heptane fraction were charged into a glass flask and chlorinated at 50° C., with an S–4 mercury lamp placed next to the flask; 0.7 gram of iodine crystals was added to the flask. Chlorination was continued until the net gain in weight was 535 grams. This is equivalent to 105 per cent chlorination based on the monochloride.

Alkylation

Into the conventional 3 liter, three-necked flask equipped with stirrer, reflux condenser, thermometer and dropping funnel were charged 515 grams (6.6 moles) benzene and 58.7 grams (0.44 mole) of aluminum chloride. Nine hundred grams of the crude chloroheptanes derived from the chlorination described above were added over a period of 100 minutes while the temperature of the contents of the flask was maintained at 40–50° C. Stirring was continued at this temperature for an additional 3 hours. After the reaction mixture had cooled, the organic layer was separated from the aluminum chloride sludge, and clarified and freed of dissolved hydrogen chloride by filtration through a mixture of Hiflo and Super Filtrol. The unreacted benzene and heptane were removed by distilling this product at atmospheric pressure to a temperature of approximately 125° C. The residue of the distillation was sulfonated.

Sulfonation

The alkylated benzenes were contacted with half their weight of 96 per cent sulfuric acid in an ice bath (5–10° C.) To the stirred contents a volume of 60 per cent oleum equivalent to that of the 96 per cent sulfuric acid originally employed, was charged. The reaction mixture was quenched and a small quantity of 91 per cent isopropyl alcohol added. After neutralization with 50 per cent by weight sodium hydroxide solution had been initiated, two layers formed, acid and sulfonic acid-oil. The acid layer was withdrawn and neutralization completed. The sulfonate solution was extracted several times with petroleum ether, then dried on a rotary drum dryer. The recovered sulfonates had wetting times of 3.0 seconds at ½ per cent, 21 seconds at ¼ per cent, and 55 seconds at ⅛ per cent.

EXAMPLE III

Heptyl and Octyl Benzene Sodium Sulfonates

Chlorination

A straight-run gasoline was fractionated and a fraction boiling from 91–130° C. and weighing 1409 grams was charged into a 5 liter three-necked flask set up in the conventional manner for chlorination with stirrer, reflux condenser, thermometer, and gas inlet tube. A 60 watt light bulb was placed next to the flask for light source. The charge was warmed to 50° C. and chlorine started through. According to the original fractionation, about ⅔ by weight of the fraction taken was heptanes and ⅓ was octanes. The chlorination was carried out at 50–60° C. until the gain in weight after nitrogen blowing was 273 grams. This corresponds to about 59 per cent of the chlorine required to form the monochloride.

Alkylation

The chlorination mixture weighing 1682 grams and containing 273 grams (7.7 moles) of chlorine was charged to a 2 liter separatory funnel. A 5 liter three-necked flask was set up with stirrer, reflux condenser, thermometer, and the 2 liter separatory funnel for addition of chlorides. To the flask was charged 600 grams (7.7 moles) of benzene and 68 grams (0.508 mole) of anhydrous $AlCl_3$. The charge was warmed to reflux with stirring (about 70° C.). The alkyl chlorides were added to the refluxing mixture over a period of 5 hours. The temperature rose slowly to 82° C. The reaction mixture was refluxed another hour at 96° C., allowed to stand overnight and the alkylate layer was decanted from the sludge. The alkylate was filtered through a mixture of 25 grams Hiflo and 50 grams Super Filtrol.

Sulfonation

One hundred fifty-nine milliliters (150 grams) of the distilled alkylate boiling 308–359° C. were mixed with 160 milliliters of liquid sulfur dioxide in a Dewar flask with a stopcock at the bottom. Thirty-seven milliliters of 60 per cent oleum were mixed with 100 milliliters of liquid sulfur

dioxide and placed in a separatory funnel. The sulfonating mixture was slowly added to the charge. The reaction mixture was run into 75 milliliters of water, warmed to 30° C., neutralized with 50 per cent by weight sodium hydroxide solution. The sulfonate solution was extracted several times with petroleum ether and dried on the rotary drum dryer. The crude dry sulfonates were mixed with 1500 milliliters of anhydrous methanol, heated to reflux, and filtered to remove inorganic salt. The filtrate was partly evaporated and dried on the drum dryer, yielding 111 grams. The resulting product gave instantaneous wetting times at 1 per cent and at ½ per cent, and 9.1 seconds at ⅛ per cent concentration.

EXAMPLE IV

Heptyl and Octyl Benzene Sodium Sulfonates

Chlorination

This operation was similar to Example III, except that 1057 grams of a fraction from Michigan straight-run gasoline (M–4 reference fuel) was used, boiling from 90–130° C. This material, based on fractionation data, was about 50 per cent by weight heptanes and 50 per cent octanes. It was chlorinated at 50–60° C. The total gain in weight due to chlorine addition amounted to 289 grams, which corresponded to 82 per cent of the amount required for monochlorination.

Alkylation

The procedure in general corresponded to that used in Example III. The charge in the flask comprised a mixture of 635 grams (8.14 moles) of benzene and 72.3 grams (0.542 mole) of anhydrous aluminum chloride. The mixture of products from the above chlorination was used. It weighed 1346 grams and contained 289 grams (8.14 moles) of combined chlorine. The reaction was carried out at reflux temperature for a total time of 5 hours. The alkylate was filtered through a mixture of 25 grams Hiflo and 50 grams Super Filtrol. The filtrate still contained hydrochloric acid so it was extracted with 55 milliliters of 2 per cent aqueous sodium hydroxide solution. The organic layer was dried with calcium chloride, filtered, and saved for distillation.

Sulfonation

The sulfonation was performed as in Example III. The charge to the Dewar flask comprised 100 milliliters (83 grams) of the fractionated alkylate boiling between 305 and 359° C. mixed with 100 milliliters of liquid sulfur dioxide. The sulfonating mixture comprised 21 milliliters of 60 per cent oleum dissolved in 90 milliliters of liquid sulfur dioxide. The reaction mixture was neutralized with 41 milliliters of 50 per cent by weight sodium hydroxide solution. The remaining operations were done as in Example III, yielding 62 grams of finished product. This material gave instantaneous wetting times at 1 and at ½ per cent concentrations, 12 seconds at ⅛ per cent, and 30 seconds at $\frac{1}{16}$ per cent.

EXAMPLE V

Mono- and Dioctyl Benzene Sodium Sulfonates

Chlorination

The chlorination was performed similar to Example III, using 1400 milliliters (1008 grams) of a fraction from Michigan straight-run gasoline (M–4 reference fuel) which boiled from 120° C. to 130° C. The chlorination was carried out at 60–70° C. and the chlorination mixture contained 47.7 per cent by weight of the chlorine theoretically required to form the monochloride.

Alkylation

The chlorination mixture was distilled under reduced pressure and the fraction boiling from 130° C. to 180° C. was used for alkylation. The alkylation procedure was similar to that used in Example III.

Charge to the flask:

252 grams (3.23 moles) of benzene
48.5 grams (0.363 mole) of aluminum chloride

Octyl chloride added: 479 grams (3.23 moles).
Temperature: 50–60° C.
Time: 4 hours.

The alkylation mixture was quenched with 200 milliliters of water, shaken in a separatory funnel, and the aqueous layer withdrawn. The organic layer was then shaken with anhydrous calcium chloride and filtered through a mixture of Hiflo-Super Filtrol. The filtrate was then fractionated under reduced pressure.

Sulfonation

These sulfonations were carried out in a manner similar to that given in Example III.

A. *Monooctyl benzene.*—The Dewar flask was charged with 100 milliliters (89 grams) of octyl benzene boiling from 236° C. to 265° C. in 100 milliliters of liquid sulfur dioxide. The sulfonating mixture was composed of a solution of 32 milliliters of 60 per cent oleum in 100 milliliters of liquid sulfur dioxide. The reaction mixture was quenched with water, neutralized with 50 per cent by weight sodium hydroxide solution, and worked up as in Example III. The yield of inorganic salt-free sulfonates was 99 grams, giving wetting times in seconds as follows:

Concentration (per cent)	1	½	¼	⅛
Wetting time (seconds)	2.9	10.4	71.3	300+

B. *Dioctyl benzene.*—The Dewar flask was charged with 37 grams of a fraction boiling from 332–359° C. from the octyl benzene alkylate and 50 milliliters of liquid sulfur dioxide. The charge was sulfonated with 9 milliliters of 60 per cent oleum mixed with 30 milliliters of liquid sulfur dioxide. The reaction mixture was then quenched with water, neutralized with 50 per cent by weight sodium hydroxide solution, and worked up in a manner similar to that used in Example III. An inorganic salt-free product resulted weighing 19 grams. This material, when dissolved in distilled water, gave the following wetting times:

Concentration (per cent)	½	¼	⅛	$\frac{1}{16}$	$\frac{1}{32}$
Wetting time (seconds)	Inst.	--	19.4	33.4	146.5

EXAMPLE VI

Mono- and Dinonyl Benzene Sodium Sulfonates

Chlorination

This operation was performed similar to the chlorination in Example III, using 1008 grams of a fraction from Michigan straight-run gasoline (M-4 reference fuel) boiling from 145° C. to 155° C. The reaction was carried out at 60–70° C, and after the chlorination was completed the reaction mixture was blown with nitrogen until it was free of dissolved hydrogen chloride and chlorine. The

gain in weight due to combined chlorine was equivalent to 53.6 per cent of the theoretical amount required for monochlorination.

Alkylation

The procedure used was similar to that used in Example III. The chlorination mixture was distilled under reduced pressure and the fraction collected having a corrected boiling range of 180–205° C. was used for the alkylation.

Charge to flask:

156 grams (2 moles) of benzene.
30 grams (0.226 mole) of aluminum chloride.

Nonyl chlorides added: 325 grams (2 moles).
Alkylation temperature: 50–60° C.
Time of reaction: 3½ hours.

The alkylation mixture was allowed to stand overnight. It was then quenched with 300 milliliters of water, shaken in a separatory funnel and the aqueous layer withdrawn. The organic layer was shaken with anhydrous calcium chloride and filtered through a blend of Hiflo-Super Filtrol. The filtrate was fractionally distilled under reduced pressure.

Sulfonation

These sulfonations were done in a manner similar to that given in Example III.

A. *Monononyl benzene.*—Charge to Dewar flask: 100 milliliters (88 grams) of nonyl benzene from the above alkylation boiling from 255 to 284° C. (corrected) and 100 milliliters of liquid sulfur dioxide. The sulfonating mixture used was a solution of 29 milliliters of 60 per cent oleum and 100 milliliters of liquid sulfur dioxide. The sulfonation mixture was quenched with 55 milliliters of water. It was then worked up as was the material in Example III. After final purification, 99 grams of inorganic salt-free sulfonates resulted. This material gave the following results using the standard wetting test procedure.

Concentration (per cent)	1	½	¼	⅛	1/16
Wetting time (seconds)	Inst.	2.4	32.3	52.4	300+

B. *Dinonyl benzene.*—The charge to the Dewar flask was 52 grams of dinonyl benzene from the above alkylation boiling from 343–384° C. and 80 milliliters of liquid sulfur dioxide. The sulfonating agent used was a solution of 11 milliliters of 60 per cent oleum in 50 milliliters of liquid sulfur dioxide. The sulfonation reaction product was worked up in a manner similar to that used in Example III, resulting in a purified product weighing 21 grams. The results of the wetting tests follow:

Concentration (per cent)	½	¼	⅛	1/16
Wetting time (seconds)	16.4	28.8	44.2	94.5

EXAMPLE VII

T-Butyl Decyl Benzene Sodium Sulfonate

Chlorination

The chlorination of n-decane was performed as usual, using 755 grams of a fraction from Michigan straight-run gasoline (M–4 reference fuel) boiling from 170 to 180° C. The chlorination was carried out at 50° C. to 60° C. and blown with nitrogen at 55° C. until it was free of hydrogen chloride and unreacted chlorine. The weight of chlorine added corresponded to 64.3 per cent of the amount theoretically required for monochlorination. The chlorination mixture was fractionated under reduced pressure.

Alkylation

The alkylation procedure was similar to that used in Example III. To the flask was charged 268 grams (2 moles) of t-butyl benzene boiling at 170° C. and 27 grams (.2 mole) of anhydrous aluminum chloride. To this stirred mixture was added slowly 352 grams (2 moles) of decyl chlorides from the above chlorination boiling (corrected) from 180° C. to 237° C. The temperature used was 50° C. to 60° C. and the total reaction time was 4 hours. The alkylate was decanted from the organic aluminum chloride complex which had settled as a viscous sludge, then filtered through a mixture of 20 grams Hiflo and 40 grams of Super Filtrol. The filtrate was fractionated at reduced pressure.

Sulfonation

The sulfonation was performed as in Example III. The charge comprised 36 grams of t-butyl decyl benzene having a corrected boiling range of 299° C. to 330° C. in 50 milliliters of liquid sulfur dioxide. The sulfonating agent was a solution of 10 milliliters of 60 per cent oleum in 30 milliliters of liquid sulfur dioxide. The sulfonation reaction mixture was quenched with 20 milliliters of water and required 17 milliliters of 50 per cent by weight sodium hydroxide solution for neutralization. The sulfonate solution was washed with petroleum ether and dried. The sulfonates were freed of inorganic salts in the usual manner using anhydrous methanol. The yield of salt-free sulfonates was 34 grams. The wetting tests gave the following results:

Concentration (per cent)	1	½	¼	1/16	1/32
Wetting time (seconds)	Inst.	Inst.	Inst.	25.2	74.7

EXAMPLE VIII

Alkyl Benzene Sodium Sulfonates

A sample of thermal gasoline having a volume of 2500 milliliters and weighing 1787 grams was fractionated at atmospheric pressure in a 10-plate laboratory column. The gasoline distilled in a range of 40° C. to 175° C. A composite of the fractions boiling from 40° C. to 135° C. was taken for alkylation with benzene. This composite comprised 52.5 per cent by weight of the total gasoline. The bromine addition value of this fraction was 65.6 and its A. P. I. gravity was 62.9. According to the former analysis, the thermal gasoline in this range was about 50 per cent olefinic, based on monoolefins.

Alkylation

A 2 liter three-necked flask was set up with a stirrer, reflux condenser, thermometer, and a 1 liter separatory funnel for addition of olefinic material. In the flask were placed 32 grams (0.236 mole) of anhydrous aluminum chloride and 184 grams (2.36 moles) of reagent benzene. In the separatory funnel was placed 427 grams (about 2.36 moles) of the thermal gasoline fraction. The charge was warmed to 36° C. with stirring and the thermal gasoline slowly added. The temperature rose to 60° C. and remained there without external heating. The olefin addition was completed over a period of 1½ hours. The reaction mixture was maintained at 50–60° C. for an additional 2 hours. After standing overnight, the alkylate was decanted from the viscous sludge layer and filtered through a mix-

ture of 15 grams of Hiflo and 30 grams of Super Filtrol. The filtrate was fractionated under reduced pressure.

Sulfonation

In an unsilvered Dewar flask was placed 100 milliliters of liquid sulfur dioxide and 63 grams of a fraction from the above alkylation having a corrected boiling range of 250° C. to 410° C. The sulfonating agent used comprised 25 milliliters of 60 per cent oleum dissolved in 75 milliliters of liquid sulfur dioxide. It was placed in a separatory funnel and slowly added to the charge. The sulfonation mixture was poured into 48 milliliters of water. This quenched mixture was warmed to 35° C. After adding 90 milliliters of 91 per cent isopropyl alcohol the neutralization was begun. An aqueous acid layer formed which was separated and discarded. The neutralization was completed using a total of 35 milliliters of 50 per cent by weight sodium hydroxide solution. The neutral sulfonate solution was extracted several times with petroleum ether to remove any unsulfonated organic material. It was then dried on the rotary drum dryer. The inorganic salts were then removed by mixing the dry product with 500 milliliters of anhydrous methanol, heating, and filtering. The filtrate was then dried on the drum dryer, yielding 60 grams of purified product. Draves tests on the product gave wetting times as follows:

Concentration (per cent)	1	½	¼	⅛	1/16
Wetting time (seconds)	Inst.	Inst.	3.7	16.0	60.5

EXAMPLE IX

MONO- AND DIHEPTYL BENZENE SODIUM SULFONATES

A sample of thermal gasoline weighing 1829 grams was fractionated at atmospheric pressure as in Example VIII. A fraction boiling from 80° C. to 108° C. was saved, comprising 10 per cent by weight of the charge. It was about 50 per cent olefinic based on monoolefins.

Alkylation

This procedure was similar to that used in Example VIII. The flask was charged with 78 grams (1 mole) of benzene and 15 grams (0.113 mole) of aluminum chloride. In the separatory funnel was placed 188 grams (about 1 mole) of the C_7 thermal gasoline fraction. The olefin was added over a period of 2 hours with continuous stirring at 50° C. The reaction mixture was stirred for an additional 2 hours. After standing overnight, it was mixed with 100 milliliters of water, placed in a separatory funnel, and the aqueous layer discarded. The alkylate was dried with anhydrous calcium chloride and filtered through a blend of Hiflo-Super Filtrol. The filtrate was fractionated.

Sulfonation

A. *Monoheptyl benzene.*—This sulfonation was performed as in Example III. The Dewar flask was charged with 22 grams of heptyl benzene boiling from 222° C. to 250° C. from the above distilled alkylate and 50 milliliters of liquid sulfur dioxide. The charge was sulfonated with a mixture of 10 milliliters of 60 per cent oleum and 30 milliliters of liquid sulfur dioxide. The remainder of the steps used was similar to Example III except the sulfonates were dried in the constant temperature oven set at 105° C. rather than on the drum dryer. The yield of purified product was 20 grams, giving the following wetting times:

Concentration (per cent.)	2	1	½	¼
Wetting time (seconds)	3.8	7.0	65.1	300+

B. *Diheptyl benzene.*—The sulfonation procedure used was similar to part A above. The sulfonatable charge comprised 12 grams of diheptyl benzene from the distilled alkylate above boiling from 352 to 392° C. and 12 milliliters of liquid sulfur dioxide. The sulfonating mixture was a solution of 5 milliliters of 60 per cent oleum in 20 milliliters of liquid sulphur dioxide. A yield of salt-free sulfonates weighing 6 grams was obtained. The wetting times were as follows:

Concentration (per cent.)	½	¼	⅛
Wetting time (seconds)	14.6	37.3	102.1

EXAMPLE X

METHYL CYCLOHEXYL BENZENE SODIUM SULFONATE

Alkylation

A 3 liter three-necked flask was set up with stirrer, reflux condenser, and separatory funnel. It was charged with 500 grams (3.75 moles) of aluminum chloride and 655 grams (8.4 moles) of benzene. In the separatory funnel was placed 342 grams (3 moles) of methyl cyclohexanol. The flask containing the charge was warmed to the reflux temperature and the alcohol added in 2 hours. After cooling, 750 milliliters of water were added to the alkylation mixture, which was then placed in a separatory funnel. The aqueous layer was withdrawn and the alkylate layer shaken with anhydrous calcium chloride, then filtered through a blend of Hiflo-Super Filtrol. The filtrate was fractionally distilled under reduced pressure.

Sulfonation

The sulfonation of these alkylate fractions was carried out as in Example III.

A. *Methyl cyclohexyl benzene.*—To the Dewar flask was charged 64 grams of methyl cyclohexyl benzene from the above alkylate boiling from 244° C. to 248° C. and 100 milliliters of liquid sulfur dioxide. The sulfonating agent was a solution of 26 milliliters of 60 per cent oleum in 75 milliliters of sulfur dioxide. The steps of quenching, neutralization, extraction with petroleum ether, drying on the rotary drum dryer, and purification were done as before. A yield of 50 grams of salt-free product was obtained having the following wetting times:

Concentration (per cent)	2	1
Wetting time (seconds	89.8	300+

B. *Di-(methyl cyclohexyl) benzene.*—Charged to the Dewar flask were 31 grams of di-(methyl cyclohexyl) benzene from the above alkylate fractionation with a corrected boiling range of 340° C. to 373° C. and 100 milliliters of liquid sulfur dioxide. This was sulfonated using 10 milliliters of 60 per cent oleum in 30 milliliters of liquid sulfur dioxide. The balance of the steps in the preparation were carried out as before, yielding 25 grams of salt-free sulfonates having the following wetting times:

Concentration (per cent)	½	¼	⅛
Wetting time (seconds)	17.3	148.1	300+

EXAMPLE XI

Diamyl Naphthalene Sodium Sulfonate

Sulfonation

Diamyl naphthalene, 161 grams, was sulfonated in 340 milliliters of liquid sulfur dioxide with 85 grams of 60 per cent oleum (60 per cent free SO_3) during about 10 to about 15 minutes. The sulfonation mixture was quenched with 107 milliliters of water, the excess sulfur dioxide evaporated at 100° F. to 110° F. and the acids neutralized with aqueous sodium hydroxide. Unsulfonated oil was removed from the mixture of sodium sulfonates by washing the crude neutralized acids with petroleum ether (boiling range 30° C. to 60° C.) in the presence of isopropyl alcohol. A yield of 161 grams of sodium sulfonates was obtained. In the Draves test these sulfonates had the following wetting times:

Concentration (per cent)	½	¼	⅛
Wetting time (seconds)	Inst.	2.9	300+

EXAMPLE XII

Alkylated Trimethyl Naphthalene Sodium Sulfonate

Alkyation

Seventeen hundred grams of a fraction of multiple pass Houdry bottoms having a boiling range of 570° F. to 600° F. and having as its primary constituents polymethyl and ethyl naphthalenes, was alkylated with 983 grams of thermal gasoline (boiling range 104° F. to 347° F.) in the presence of 34 grams of anhydrous aluminum chloride for 6 hours at about 104° F. The alkylation mixture was topped to remove unreacted gasoline and the topped alkylation mixture distilled under reduced pressure.

Sulfonation

A fraction of the alkylate boiling at about 617° F. to about 646° F. (corrected to atmospheric pressure) in the amount of 104 grams was sulfonated with 45 grams of oleum (68 per cent free SO_3) in 250 milliliters of liquid sulfur dioxide during a period of about 12 minutes. The sulfonation mixture was quenched with 46 grams of ice, warmed to about 130° F. to remove excess sulfur dioxide, and neutralized. The crude neutralized product was purified in a manner similar to that described in Example XI. A yield of 75 grams of purified sodium sulfonates was obtained. These sulfonates had the following wetting times in the Draves test:

Concentration (per cent)	2	1	½	¼	⅛
Wetting time (seconds)	Inst.	1.3	4.9	22	158

EXAMPLE XIII

Dibutyl Trimethyl Naphthalene Sodium Sulfonate

Alkylation

Seventeen hundred grams of a fraction of multiple pass Houdry bottoms having a boiling range of 530° F. to 540° F. was alkylated with 670 grams of diisobutylene in the presence of 33 grams of anhydrous aluminum chloride for about 6 hours at a temperature of about 86° F. to about 95° F. The alkylation mixture was topped to remove unreacted diisobutylene and the topped alkylation mixture was distilled under reduced pressure. A fraction of the alkylation mixture having a boiling range of 648° F. to 698° F. (corrected to atmospheric pressure) was sulfonated with 120 grams of oleum (30 per cent free SO_3) in 250 milliliters of liquid sulfur dioxide during a period of about 15 minutes. The sulfonation mixture was quenched with 120 milliliters of water, the excess sulfur dioxide evaporated at about 100° C. to 110° C. and the material purified in a manner similar to that described in Example II. In the Draves test these sulfonates had the following wetting times:

Concentration (per cent)	½	¼	⅛
Wetting time (seconds)	Inst.	4.8	20

One of the distinct advantages of the present invention is illustrated by the following examples. As has been emphasized hereinbefore, the art has been limited in its sources of sulfonatable material. For example, the art has been limited to kerosene as a cheap source of alkylating material providing alkyl chains of 14 to 16 carbon atoms. In order to prepare sulfonatable alkyl aromatic hydrocarbons, benzene from another source has been alkylated with the kerosene. Now, as a result of the present discovery that polyalkylated aromatic hydrocarbons of the type disclosed hereinbefore when sulfonated are exceptional wetting agents, it is possible to derive the aromatic hydrocarbons and the alkylating material both from one source, thermal and catalytically cracked gasoline, and other mixtures containing olefinic and aromatic hydrocarbons.

Thermal gasoline suitable for the preparation of polyalkyl aryl alkali metal sulfonates is characterized by the following properties:

Gravity, A. P. I. °	44 to 67
A. S. T. M. distillation range, °F	82 to 426
Bromine No	41 to 81
Weight per cent olefin	29 to 60
Volume per cent aromatic (C_6 to C_{11}) hydrocarbons	6 to 23

A gasoline of the general type described hereinbefore is reacted in the presence of an alkylating agent such as sulfuric acid, hydrogen fluoride, aluminum chloride and the like under alkylating conditions. The olefins of the gasoline alkylate the aromatic hydrocarbons of the gasoline to provide an alkylation product containing the alkymer, unreacted hydrocarbons, etc. The alkylation product is separated from the catalyst, neutralized in the customary manner and contacted with clay as usual. The neutralized and clay treated alkylate is then topped to remove unreacted hydrocarbons and the topped crude alkylate distilled under reduced pressure. The alkylate fraction is then sulfonated in any suitable manner. The sulfonated material is separated from the sulfonating agent, neutralized, washed to remove unsulfonated material and dried. The foregoing method of producing the novel wetting agents is illustrated by the following non-limiting examples.

EXAMPLE XIV

A pressure resistant container of suitable capacity was charged with about 6.25 pounds of anhydrous hydrogen fluoride. During a period of about 2 hours about 22.7 pounds of thermal gasoline containing about 34 per cent by weight olefins (C_5 to C_{11}) and about 7.3 per cent by volume aromatic hydrocarbons (C_6 to C_{11}) were pumped in whilst the reaction mixture was stirred and temperature of the mixture held at about 65 to about 70 degrees Fahrenheit. After all of the

gasoline had been added the reaction mixture was stirred for about 10 minutes. The mixture was then allowed to stratify to form a catalyst layer and a hydrocarbon layer. The major portion of the catalyst layer was withdrawn. The alkylate layer was neutralized with aqueous potassium hydroxide to remove residual hydrogen fluoride and the alkylate layer contacted with 1500 milliliters of fresh burnt 30/60 mesh Attapulgus clay. The treated alkylate mixture weighed 19.5 pounds.

The treated alkylate was then topped to 430° F. (a temperature about 40 degrees higher than the end point of the gasoline) and the still residue distilled under a pressure of 92 to 6 millimeters of mercury to 750° F. (corrected to 760 millimeters of mercury). The alkylate boiling through the range 430° F. to 750° F. at 760 millimeters of mercury corresponded to 31.3 per cent by weight of the clay treated (percolated) alkylation mixture; the residue above 750° F. was 2 per cent by weight of the percolated alkylation mixture.

A portion of the alkylate fraction boiling at 430° F. to 750° F. and weighing about 1.8 pounds was pretreated with 0.19 pound of 100 per cent H_2SO_4 to remove polymerizates and the acid sludge discarded. The treated alkylate was then sulfonated at about 50° F. to about 60° F. by about 2 pounds of oleum (25 per cent free SO_3). The sulfonation mixture was quenched with ice. An aqueous sulfuric acid layer settled out and was separated from the sulfonic acid layer. The sulfonic acid layer was neutralized with aqueous 20 per cent caustic soda.

The solution of the alkaryl sodium sulfonates was washed several times at about 175 degrees Fahrenheit with a solvent for unsulfonated material. Intermediate naphtha having a boiling range of about 190° F. to about 315° F. has been found satisfactory. The resulting extracted aqueous solution of alkaryl sodium sulfonates was dried. The yield of dried sulfonates weighed about 1.87 pounds and contained about 78.8 per cent by weight of active ingredient.

The sulfonates so produced had the following Draves wetting tests:

Concentration alkaryl sodium sulfonate per cent weight	Wetting time, seconds
0.5	4.5
0.25	18.0
0.125	41.0

The naphtha washings from the sulfonate solution were combined, water washed and topped to 410° F. The residue of unsulfonated alkylate was 0.6 pound. A portion of this residue was treated with an excess of 25 per cent oleum at about 50° F. to about 60° F. and found to be about 53 per cent sulfonatable under these conditions. Therefore, the original alkylate fraction had a sulfonatable content of about 84 per cent.

EXAMPLES XV, XVI and XVII

The results obtained by autoalkylating a similar hydrocarbon oil containing both alkylatable and alkylating hydrocarbons in the presence of other respresentative alkylation catalysts are collected in Table VII:

TABLE VII

Example No.	Weight of Charge, Gms.	Boiling Range of Charge, ° F.	Catalyst	Temperature of Alkylation, ° F.	Wt. % yield of alkylate boiling above end point of charge	Wt. % of alkylate (518–734° F.) Sulfonated	Draves Tests seconds at concentration of—		
							0.5%	0.25%	0.125%
XV	500	120–300	100 ml. 96% H_2SO_4	32–40	32	25	2.3	14	41
XVI	1,000	120–300	32 g. $BF_3.H_2O$	120–170	29	28	2.8	12	22
XVII	1,000	120–430	50 g. $AlCl_3$	120–190	32	34	------	9.1	26

The data in Table VIII illustrates the results which can be obtained employing gasoline as the sole source of the alkylatable and alkylating material and employing an aromatic petroleum fraction such as "Sovasol" No. 73 as a fortifying agent:

TABLE VIII

Example No.	Yield of Alkylate above end point of gasoline	Wt. percent Residue above 750° F.	Boiling Range Alkylate Sulfonated	Wt. percent of Alkylate Sulfonated	Wt. percent of Alkylate Sulfonatable	Wt. percent [1] Yield of pure Sulfonates	Percent Active Ingredient	Draves Tests seconds at percent concentration of active ingredient		
								0.5	0.25	0.125
	Percent		° F.							
XVIII [2]	44	4.7	410–662	82	87.7	103.2	81.9	3.4	14	39
			410–750	76.2	87.9	75.5	80.3	4.5	15	46
			527–750	77.1	86.7	84.0	79.0	3.4	9.6	30
XIX [3]	31.3	2.0	430–662	67.0	86.7	85.0	82.8	6.7	22	75
			430–750	65.9	84.0	82.2	78.8	4.5	18	41
			527–750	73.3	88.4	86.4	84.8	3.5	8.7	35
XX [4]	30.9	2.9	403–662	62.1	83.9	73.2	81.8	5.5	32	211
			403–750	71.1	87.2	82.2	84.2	5.5	20	210
			527–750	73.2	89.2	77.2	83.5	2.4	8.8	33
XXI [5]	27.9	0.5	430–662	68.6	86.8	97.2	81.3	3.3	16	141
			430–750	76.9	92.2	100.7	84.0	5.6	18	89
			527–750	76.1	92.4	81.4	78.7	Inst.	8.9	24

[1] Based on weight of alkylate charged to sulfonation.
[2] 2 parts by weight deep cracked thermal gasoline (60% olefins) and 1 part by weight aromatic petroleum stock "A," [B. R. 190–285° F. aniline point 104° F. (max.)] alkylated.
[3] Thermal gasoline autoalkylated.
[4] Polyform gasoline autoalkylated.
[5] 4 parts by weight thermal gasoline and 1 part aromatic petroleum stock "A."

The data contained in Tables VII and VIII establish that any alkylation catalyst can be used in the step of auto-alkylation prior to sulfonation. Furthermore, those skilled in the art will understand that any mixture of hydrocarbons containing olefins having 4 to 10 carbon atoms and C_6 to C_8 mononuclear aromatic hydrocarbons or C_{10}

to C_{17} polynuclear aromatic hydrocarbons can be used. It will also be understood by those skilled in the art that hydrocarbon mixtures having a deficiency in olefinic or aromatic hydrocarbons of the types described hereinbefore may be fortified by the addition of the necessary amount of hydrocarbon of the type necessary to produce an effective amount of sulfonatable mononuclear alkaryl hydrocarbon having at least two and not more than three alkyl groups and/or polynuclear alkaryl hydrocarbons having 4 to 6 alkyl groups. Thus, a cracked gasoline and an aromatic petroleum stock may be mixed and auto-alkylated or benzene may be mixed with cracked gasoline and the mixture autoalkylated.

We claim:

1. As a new article of manufacture, a wetting agent comprising a mixture of mono- and dialkyl aryl alkali metal sulfonates having a wetting time in the Draves test at 0.5 per cent concentration by weight in excess of ten seconds and sufficient of at least one polyalkylated aryl alkali metal sulfonate selected from the group consisting of di- and trialkyl aryl alkali metal sulfonates having not less than 9 and not more than about 27 alkyl carbon atoms to provide a wetting agent having a wetting time in the Draves test at 0.5 per cent of not more than about 10 seconds.

2. As a new article of manufacture, a wetting agent comprising a mixture of mono- and dialkylated aryl alkali metal sulfonates having an unsatisfactory wetting time in the Draves test and sufficient of at least one polyalkylated aryl alkali metal sulfonate to provide a composite wetting agent having a satisfactory wetting time in the Draves test, said polyalkylated aryl alkali metal sulfonate being selected from the group consisting of di- and trialkyl aryl alkali metal sulfonates having not less than 9 and not more than about 27 alkyl carbon atoms.

3. As a new article of manufacture, a wetting agent comprising about 10 per cent to about 50 per cent diheptyl benzene alkali metal sulfonate and about 90 per cent to about 50 per cent monoheptyl benzene sodium sulfonate.

4. As a new article of manufacture, a wetting agent comprising a mixture of mono-, di- and trialkyl benzene alkali metal sulfonates having a satisfactory wetting time in the Draves test, the alkyl groups of said alkyl benzene sulfonates being derived from gasoline having a boiling range of about 80 degrees centigrade to about 110 degrees centigrade.

5. As a new article of manufacture, a wetting agent comprising a mixture of mono-, di- and trialkyl benzene alkali metal sulfonates having a satisfactory wetting times in the Draves test, the alkyl groups of said alkyl benzene sulfonates being derived from predominantly paraffinic kerosene boiling between 180 degrees and 280 degrees centigrade.

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