Sulfonation and Sulfation with Sulfur Trioxide

EVERETT E. GILBERT, BENJAMIN VELDHUIS, EMERY J. CARLSON, AND SILVIO L. GIOLITO[1]
General Chemical Division, Allied Chemical & Dye Corp., Laurel Hill, L. I., N. Y.

ALTHOUGH sulfur trioxide is theoretically the most direct possible reagent for the sulfonation or sulfation of organic compounds, its practical use by industry in the past has been extremely limited. One reason for this situation is the violence of its reaction with many organic compounds compared to the behavior of other sulfonating agents, but the chief explanation lies in the strong tendency of liquid sulfur trioxide to polymerize to the solid alpha modification, which has precluded shipment and handling of sulfur trioxide as a practical article of commerce. Manufacturers of sulfuric acid, of course, have sulfur trioxide available as a dilute gas from the contact process or can store it satisfactorily as a liquid in warm tanks. On the other hand, the many sulfonators who are not also acid manufacturers would be forced to obtain sulfur trioxide by distillation from oleum; this method involves an unattractive spent acid problem which has discouraged its use except as necessary.

It has therefore long been recognized that development of a liquid sulfur trioxide of such stability as to allow normal shipment and handling could be of substantial commercial importance. Many standard sulfonation and sulfation reactions yield residual spent acid, which not only entails added cost and freight for the excess acid purchased, but creates a waste disposal problem in the face of increasingly stringent legislation, and involves greater acid consumption despite an increasing sulfur shortage. Liquid sulfur trioxide is the most economical possible form of sulfonating agent for shipment, and—from the chemical standpoint—the most efficient to use, as it eliminates or reduces the formation of spent acid. In addition, the use of sulfur trioxide should entail less reaction volume and more rapid throughput.

With these considerations as background, a search was undertaken for means which would stabilize sulfur trioxide in the liquid form. This study finally led to development of a product, Sulfan stabilized liquid sulfur trioxide, which has been satisfactorily handled and shipped in ampoules, drums, and tank cars (*36–38*). Industrial bulletins have been made available on its physical properties (*19*), and on its storage, handling, and use (*20*). Several of the pertinent physical properties of Sulfan, which are also those of the liquid or icelike form of sulfuric anhydride, are listed in Table I.

TABLE I. PHYSICAL PROPERTIES OF SULFUR TRIOXIDE (LIQUID FORM)

Boiling point, ° C.	44.8
Melting point, ° C.	16.8
Density (20° C.)	1.9224
Specific heat, cal./gram at 25–35° C.	0.77
Heat of dilution, cal./gram	504
Heat of vaporization, cal./gram	127.4
Viscosity, centipoises at 30° C.	1.590 (*21*)

After a commercially stable liquid sulfur trioxide had been developed, it became evident that insufficient information was available on its use as a sulfonating agent for organic compounds to allow immediate introduction as an industrial reagent of choice. Scattered data were available on sulfonation with sulfur trioxide as a gas (in the form of contact process converter gas, or as vaporized from oleum), but direct use of the liquid had been studied very little, and this form is preferred wherever possible. Accordingly, an exploratory study was undertaken of various possible techniques for its use as a practical sulfonating agent. The purpose of this report is to present some of the results obtained during that study. Except for the case of dodecylbenzene detergent alkylate sulfonation, involving over a hundred laboratory experiments, these results are preliminary in nature; emphasis is placed upon advancing the study of each reaction to the point where some promise appears to be shown, rather than to the final stage of a completely finished laboratory process in any particular case.

GENERAL DISCUSSION OF TECHNIQUES

A variety of procedures appears possible for conducting sulfonations with sulfur trioxide. Those methods for which specific illustrations are given in detail below are as follows:

Liquid (as Sulfan). Liquid sulfur trioxide added to the undiluted liquid (or molten) organic compound.
Liquid sulfur trioxide added to the organic substance slurried or dissolved in a solvent.
Organic substance added to undiluted sulfur trioxide or (for preparation of sulfonyl chlorides) to a mixture of liquid sulfur trioxide and chlorosulfonic acid.
Vapor. Undiluted, or diluted with dry air and passed into the undiluted liquid organic substance.

Use of sulfur trioxide in indirect form as chlorosulfonic acid, with recycle of liberated hydrogen chloride, is also discussed.

In the experimental work reported below, the commercial product Sulfan was used in all cases. To obtain sulfur trioxide in vapor form the liquid commercial product was distilled.

Whenever applicable, the direct use of the commercially available liquid form of sulfur trioxide is the simplest method, as installation of a vaporizer is obviated. In addition, heating and cooling requirements are less when using the liquid form, as the latent heat of evaporation is not involved as in the case of the vapor. (These factors are discussed more fully below.)

Although the total heat evolved in sulfonating with liquid sulfur trioxide is less than with the vapor, the vapor has been found to be a milder reagent in practice and is applicable in cases where the liquid form leads to formation of excessive color or other evidences of decomposition. This apparent paradox can be explained by the greater dispersion of the vapor as opposed to the liquid, which tends to react locally in spite of efficient agitation or extreme cooling of the compound being sulfonated.

USE AS LIQUID

Direct mixing of the liquid sulfur trioxide with the organic compound being sulfonated is the preferred technique whenever possible.

Although liquid sulfur trioxide is admittedly a strong reagent—sufficiently so to ignite some organic materials (such as excelsior and sawdust) under specific conditions—it may be added dropwise to certain organic compounds with only slight decomposition (as indicated by color formation), provided efficient agitation and cooling are employed. Glacial acetic acid and dioxane are cases in point. [In the case of dioxane, the literature erroneously reports (*56*) that even when the milder vapor form is used, an inert diluent is necessary to prevent excessive color formation. Another reference (*51*) discloses apparently successful **addition** of

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[1] Present address, Stauffer Chemical Co., Inc., Chauncey, N. Y.

TABLE II. SULFONE FORMATION WITH AROMATIC HYDROCARBONS

Expt. No.	Hydrocarbon[a]	Moles of Reactants		Order of Addn.[b]	Reaction Conditions		Sulfone Yield[c]	Remarks
		Hydrocarbon	SO_3		Temp., ° C.	Time, hours		
1	Benzene	2.0	1.0	A	20–30	0.5	17.5	....
2	Benzene	1.5	1.5	..	20–56	0.3	15.0	Vapor passed into hydrocarbon
3	Benzene	1.0	1.0	B	22–40	0.8	7.5	....
4	Benzene	2.0	2.0	C	38–50	2.0	5.2	Heel used[d]
5	Benzene	2.0	2.0	C	38–50	2.0	8.1	Heel used[e]
6	Toluene	2.0	2.0	A	50–55	0.5	9.7	[f]
7	*p*-Xylene	2.0	2.0	A	55–70	0.5	5.1	[g]
8	Chlorobenzene	5.0	5.0	A	27–120	1.5	13.9	....

[a] Grades of reagents used: benzene, Barrett industrial pure; toluene, Barrett nitration grade; *p*-xylene, 95%, Oronite Chemical Co.; chlorobenzene, technical, Dow Chemical Co.

[b] A. Liquid sulfur trioxide added to hydrocarbon. B. Hydrocarbon added to liquid sulfur trioxide. C. Hydrocarbon and liquid sulfur trioxide added simultaneously to "heel" of benzenesulfonic acid.

[c] Sulfone yields expressed as % liquid sulfur trioxide used reacting to yield sulfone by equation: $2RH + SO_3 \rightarrow R_2SO_2 + H_2O$. Sulfone isolated by drowning reaction mixture in water to complete precipitation, and evaporating any unreacted hydrocarbon in vacuo.

[d] Technical benzenesulfonic acid (600 grams) used as heel, yield calculated on heel-free basis.

[e] Expt. 5 same as Expt. 4, except that 200 grams of heel used.

[f] Product analysis: 76.4% sulfonic acids; 14.0% sulfone; 5.0% unreacted toluene; 4.6% sulfuric acid. Sulfone identified as 4,4′ by m.p. [lit. 158–9° C. (*2*), found 158–9° C. (uncorr.)]. Sulfonic acids contained principally 4 isomer, as shown by m.p. of aniline salt [lit. 238° C., (*15*), found 234° C. (uncorr.)], and *p*-toluidine salt [lit. 198° C., (*15*), found 194° C. (uncorr.)].

[g] Product analysis: 81.5% sulfonic acids; 7.6 sulfone; 7.3 unreacted xylene; 3.6 sulfuric acid. Sulfone identified as derived from *p*-xylene by m. p. [lit. 142° C., (*43*), found 143–5° C. (uncorr.)]. Sulfonic acids contained principally *p*-xylene monosulfonic acid, as shown by m. p. of *S*-benzyl thiouronium salt [lit. 181–2° C., (*10*), found 178–80° C. (uncorr.)].

the liquid to the dioxane-solvent mixture. In the present study only slight development of color was noted upon the addition of liquid sulfur trioxide to dioxane.]

With certain other organic compounds, color formation is appreciable, but still not indicative of a prohibitive degree of decomposition.

Aromatic Hydrocarbons. Direct sulfonation of aromatic hydrocarbons with liquid sulfur trioxide in the absence of an inert solvent has not been studied previously. Benzene (*35*) and toluene (*32*) have been made to react with the vapor, and benzene, toluene, chlorobenzene, and naphthalene have been treated with sulfur trioxide dissolved in chloroform (*14, 33, 57*). Benzene has been made to react with sulfur trioxide in liquid sulfur dioxide (*8, 9, 23, 33*) and with dioxane–sulfur trioxide complex (*57*). Benzene as vapor reacted with sulfur trioxide as vapor gives a high yield (about 50%) of sulfone (*7*).

Accordingly, a series of exploratory experiments was undertaken involving direct dropwise mixing of the two liquid reagents, and one experiment was run using sulfur trioxide as vapor. The experimental technique involved dropwise addition of one liquid to the other in a reactor flask equipped as shown in Figure 2, except that the gas input tube was replaced by a dropping funnel. External cooling was used in all cases except in that of chlorobenzene, where the temperature was allowed to rise. The results are recorded in Table II.

No violent decomposition or charring was noted in these experiments even when benzene was added to liquid sulfur trioxide. The crude sulfonic acids were red, except in the case of chlorobenzene, where the product was yellow. The toluene and *p*-xylene reaction mixtures were neutralized and dried to light gray sodium salts.

Conclusions were drawn as follows. Addition of benzene to the liquid yields less sulfone than the reverse procedure; the same observation was reported using sulfur dioxide as solvent (*33*). Sulfone formation from benzene is high using sulfur trioxide as either liquor or vapor, and in general agrees with the figures given in the literature (*35*). It can be substantially reduced by use of the "heel technique," but is still higher than as reported using solvents.

Acetanilide (Sulfonyl Chloride). Aromatic sulfonyl chlorides are ordinarily prepared by adding the organic compound to be sulfonated to chlorosulfonic acid, hydrogen chloride being evolved in the first step of this two-step reaction (*24*). Because the first step involves sulfonation only, it has been suggested (*11*) that use of a mixture of sulfur trioxide and chlorosulfonic acid could lead to the same result without formation of hydrogen chloride, as shown in the following equation for the specific case of acetanilide:

$$CH_3CONHC_6H_5 + SO_3 \longrightarrow CH_3CONHC_6H_4SO_3H \qquad \text{Step I}$$

$$CH_3CONHC_6H_4SO_3H + ClSO_3H \longrightarrow CH_3CONHC_6H_4SO_2Cl + H_2SO_4 \qquad \text{Step II}$$

In view of the fact that such a mixture is conveniently prepared by simple mixing of liquid sulfur trioxide and chlorosulfonic acid, and the likelihood that the preparative details given in the literature (*11*) would not give optimum yields, such a sulfonation of acetanilide using the mixture was carried out on a comparative basis with chlorosulfonic acid.

Acetanilide was converted to the sulfonyl chloride using the published procedure (*50*), except that 1 mole of liquid sulfur trioxide was substituted for 1 mole of chlorosulfonic acid per mole of the organic substance treated. The same reaction conditions were used throughout. Acetanilide (67.5 grams, 0.5 mole, Baker and Adamson powder U.S.P.) was added slowly with cooling and agitation to a mixture of chlorosulfonic acid (232 grams, 2 moles, Monsanto technical grade) and liquid sulfur trioxide (40 grams, 0.5 mole) over a period of 0.5 hour, at a temperature of 10° to 15° C. The reaction mixture was then heated 2 hours on the steam bath at 60° to 80° C. to complete reaction. No hydrogen chloride was evolved during reaction or heating. Drowning on ice gave a yield of 95 grams of crude dried product, light gray in color, melting at 138° to 145° C. (uncorrected), compared to 90 to 95 grams reported for the chlorosulfonic procedure (*50*). (The literature melting point for the recrystallized product is 149° C.)

The general procedure has also been found applicable to other benzene derivatives such as chlorobenzene and nitrobenzene. As when chlorosulfonic acid is used, there is some by-product sulfone formation.

Benzoic Acid. Benzoic acid has been partially sulfonated (*31*) by the introduction of sulfur trioxide vapor into the molten acid at 140° C. It has also been sulfonated with oleum (*49*). Direct addition of liquid sulfur trioxide to the molten acid has not been reported.

Liquid sulfur trioxide (176 grams, 2.2 moles) was added dropwise over a 23-minute period to molten benzoic acid (244 grams, 2.0 moles of Baker and Adamson reagent), maintained at 125° to 140° C. during addition, which was carried out in a reactor flask equipped as shown in Figure 2, except that the gas input tube was replaced by a dropping funnel. (During addition each drop of sulfur trioxide produced a hissing sound upon striking the benzoic acid, but no charring was noted, as the reaction mixture was yellow to red throughout.) After addition was completed, the reaction mixture was digested for 1 hour at 130° to 150° C. Yield was 418 grams (99.5% based on total reagents). The reaction mixture solidified on standing at room temperature to a yellow-pink solid. It was completely water-soluble; total acidity, basis sulfobenzoic acid, was 107% of theory; sulfuric acid content was 6.9%. The crude *S*-benzyl thiouronium salt melted at 155–8° C. (uncorrected); (literature 163–4° C., *60*).

It appears noteworthy in the above experiment that negligible loss of sulfur trioxide occurred, even though the reaction temperature was considerably above the boiling point (44.8° C.).

Toluic and chlorinated benzoic acids have been successfully sulfonated in a similar manner.

Salicylic Acid. This sulfonation has in the past been conducted with concentrated sulfuric acid in large excess (*45*). Other phenolic compounds have been sulfonated with sulfur trioxide vapor using a slurrying medium (*58*). Salicylic acid, being unstable at elevated temperatures, cannot be sulfonated in molten form as described above for benzoic acid; the solid acid has been reacted with sulfur trioxide vapor (*1*, *6*, *39*).

Liquid sulfur trioxide was added dropwise over a 13-minute period to salicylic acid (100 grams, 0.73 mole Baker and Adamson reagent) suspended in tetrachloroethylene (300 grams) in an agitated 3-necked flask. No cooling was used, and the temperature rose from 29° to 100° C. during addition. No difficulty was experienced with caking or sticking. After addition, the reaction mixture was refluxed gently for 3 hours. After cooling, the solvent was filtered from the suspended sulfosalicylic acid. The crude yellow product was dried in vacuo to remove adhering tetrachloroethylene. The yield of a product with 98% of the calculated acid value was nearly quantitative. One recrystallization from water yielded a hydrated product melting at 106–108° C. (uncorrected); the literature (*28*) gives 105–108° C.

Long-Chain Saturated Acids. Direct sulfonation of long-chain saturated fatty acids with sulfur trioxide has long been known. Sulfur trioxide may be passed into the molten acid (*27*), but use of a solvent such as liquid sulfur dioxide (*40*) or carbon tetrachloride (*26*) is preferred. With the latter solvent, not only is use of the vapor form of sulfur trioxide stipulated for sulfonation of an industrial grade of palmitic acid, but a specific warning is given against allowing any adventitious drops of the liquid to contact the solution during the gassing operation (*26*).

On the other hand, it has been found in the present study that the liquid form can be used for the sulfonation of a variety of long-chain fatty acids. The technique is generally the same as that described above for salicylic acid. Details of the procedure, using tetrachloroethylene as slurrying medium, have been reported by Stirton and coworkers (*53*), who present analytical data for the lauric, myristic, palmitic, and stearic derivatives. The *n*-butyl and *n*-amyl esters, as well as the triethanolamine salts, were prepared from sodium sulfopalmitate. The series was studied from the standpoint of water solubility, wetting properties, foaming, and detergency in comparison with established detergents (*53*).

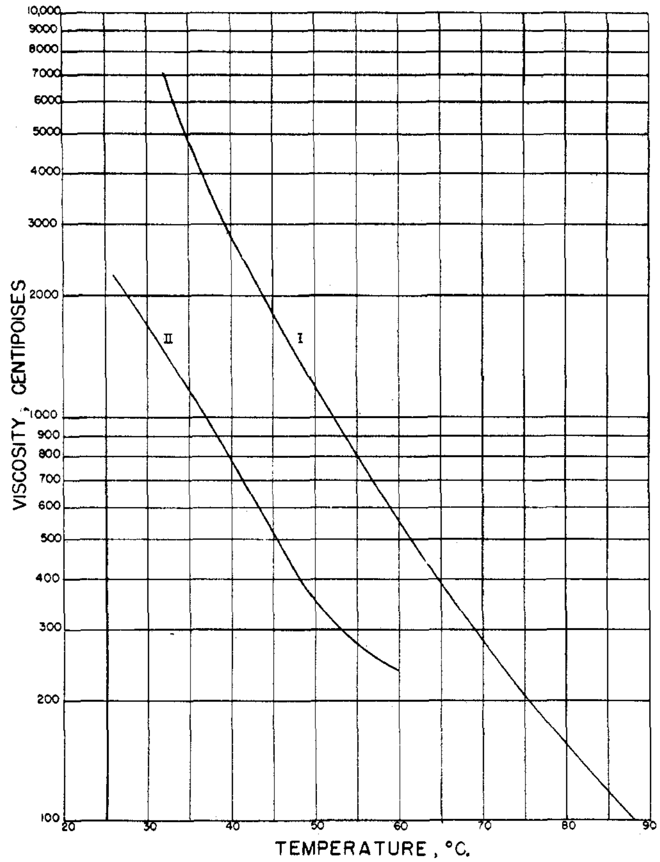

Figure 1. Viscosity-Temperature Relationship for Dodecylbenzenesulfonic Acid

I. Prepared with sulfur trioxide vapor (*21*)
II. Prepared with 20% oleum, with layer separation (*41*)

Carbon tetrachloride may be substituted for tetrachloroethylene as reaction medium in this sulfonation. Although Stirton and coworkers used purified fatty acids, the authors have found that technical grades may be used—for example, a technical grade of palmitic acid (Neo-Fat No. 1-56, Armour and Co., iodine value 3, oleic acid content 4.0%) yielded a cream colored sodium salt after one recrystallization from water.

USE AS VAPOR

Below are presented specific examples of the use of sulfur trioxide in the form of vapor for sulfonation, dry air being used as carrier gas.

DODECYLBENZENE DETERGENT ALKYLATE

Several brands of long-chain alkylated benzene hydrocarbons ("dodecylbenzene detergent alkylate") have in recent years become available for conversion, by sulfonation followed by neutralization, into widely used industrial and household detergents. These materials are ordinarily sulfonated with 20 to 22% oleum (*41*, *52*). The excess acid used may then be largely separated as spent acid by dilution with water and layering; neutralization of the organic layer and drying yield a product of 85 to 90% active ingredient content. Neutralization of the entire sulfonation mass yields a "low active" product, containing from 40 to 60% sulfonate, most of the remainder being sodium sulfate. Both of these operating procedures are objectionable, as the former yields spent acid, and the latter forms sodium sulfate in situ at a cost often higher than the purchase price of the material as such. Sulfonation using sulfur trioxide overcomes these difficulties, as a "high active" product is formed directly without the necessity for layering or the formation of spent acid.

Sulfonation of long-chain alkylated benzenes with sulfur trioxide is known (*5*, *17*, *18*, *34*, *41*, *59*). Use of liquid sulfur dioxide as the sulfonation solvent has been found to give satisfactory results (*5*, *42*). Direct passage of the vapor, diluted with air or nitrogen, into the hydrocarbon has also been cited (*4*, *18*, *34*), preferably below 40° C. (*59*).

Preliminary experiments involving direct addition of liquid sulfur trioxide to the hydrocarbon—the preferred procedure for introducing the sulfur trioxide—showed no promise even with extreme cooling and excellent agitation, as the neutralized slurry was dark in color and had a high free oil content. However, introduction of the vapor gave more promising results, and this approach was developed further.

It was soon noted that, although unsulfonated dodecylbenzene has a low viscosity and is therefore easily agitated, the sulfonic acid is sufficiently viscous below about 45° C. to render agitation, and therefore heat removal, somewhat difficult. In Figure 1 (curve I) is presented the viscosity-temperature relationship for dodecylbenzene sulfonic acid (prepared as detailed below), using a Brookfield viscometer (spindle No. 3, 12 to 60 r.p.m.). Curve II, taken from the literature (*41*) and included for comparison, applies to the concentrated dodecylbenzenesulfonic acid obtained by water dilution and layer separation in the oleum process. Approximate viscosities of the reaction mixtures in the oleum process determined at the sulfonation temperature of 25° C. have been variously reported as 500 to 800 (*41*) and 1500 centipoises (*52*), which are much lower than the figure for the sulfur trioxide process at the same temperature. However, as the sulfur trioxide process is operable at 50° to 60° C. (as explained more fully below), the viscosity range encountered in practice is about the same (550 to 1200 centipoises) for both processes. The difference in the viscosities of the sulfonic acids prepared by the two procedures is thought to result from the high sulfuric acid content (ca. 12%) of the sulfonate prepared with oleum compared with that using sulfur trioxide.

Efficient heat removal is especially important in sulfonating with sulfur trioxide vapor, as more heat is evolved than with the standard sulfonation using 20% oleum. In Table III are presented comparative data for the two processes.

In comparing the above data with those previously available (*20*, *25*), it will be noted that the more recent value for the heat of sulfonation with sulfur trioxide vapor is somewhat higher than the earlier figure of 794 B.t.u. (*25*) per pound of sulfur trioxide, while the three values for oleum in Table III generally agree with each other in being much higher than the previously quoted figures [206 and 215 B.t.u. per pound of sulfur trioxide] (*20*, *25*). It thus appears that sulfonation with sulfur trioxide vapor, although considerably more exothermic than with oleum, is at less of a comparative disadvantage in this respect than previously indicated.

TABLE III. HEATS OF SULFONATION OF DODECYLBENZENE

Sulfonating Agent	Ratio[a]	Heat of Sulfonation, B.t.u./Lb. Alkylate	Heat of Sulfonation, B.t.u./Lb. Effective SO_3[b]	Reference
20% oleum	1.25	170	502	(*21*)
		183 ± 8	542 ± 24	(*52*)
22% oleum	1.02	200	582	(*41*)
SO_3 vapor	0.38	306	905	(*21*)

[a] Parts by weight of sulfonating agent per part of dodecylbenzene.

[b] Calculated from figure in adjacent column assuming 0.337 pound of effective sulfur trioxide required per pound of dodecylbenzene (molecular weight 237).

Sulfonation with sulfur trioxide vapor at a temperature above 50° C., highly desirable for lowered viscosity with consequent efficient agitation and efficient heat removal, was found to be practical, since the sulfonic acid is stable at this elevated temperature during the time required for sulfonation.

Two laboratory processes were developed incorporating this principle—one comprising introduction of the vapor into the alkylate with agitation and cooling in a 3-necked glass laboratory flask, the second involving passage of the vapor into the alkylate in a circulating system equipped with external cooling ("cyclic" sulfonation). Similar results were obtained with both methods, except that a slightly lighter colored product (aqueous slurry of the sodium salt) was produced by the flask procedure. [This is presumed to be attributable to greater dilution of sulfur trioxide attainable in the vaporizing system used with the flask procedure, as the best color resulted when an input gas low in sulfur trioxide was used (about 10%, as discussed more fully below)].

Flask Sulfonation. RAW MATERIALS. Liquid sulfur trioxide 147 grams (1.84 moles). Alkylate, 420 grams (1.77 moles, basis molecular weight 237). Dry air, 850 liters per hour (92% of mixture).

PROCEDURE. After the apparatus had been assembled (Figure 2), the liquid sulfur trioxide was charged to the vaporizer and introduction of a slow stream of air was begun. The agitator for the reactor was started (1000 r.p.m.), and the alkylate was poured all at once into the reactor through the opened gas exit neck. The air rate was then increased to 850 liters per hour, and gentle heating of the vaporizer with a small free flame was begun, to distill the sulfur trioxide (boiling point 44.8° C.). The reaction temperature at the beginning was room temperature (30° C.) and was allowed to rise gradually to 55° to 60° C. with the application of the cooling bath as necessary to maintain this temperature. The sulfonation time was about 30 minutes. The sulfonic acid weighed 562.5 grams (loss 4.5 grams), and was clear to light brown in color.

A portion (474 grams) of the reaction mixture was immediately neutralized by addition to 600 grams of 10% sodium hydroxide, keeping the temperature at 40° to 50° C. by external cooling. Excess 10% caustic (50 grams) was then added to ensure a final neutral product, as otherwise a slow drift to the acid side occurred. The slurry was light cream in color and could be bleached to near white with sodium hypochlorite, as detailed below.

Cyclic Sulfonation. RAW MATERIALS. Liquid sulfur trioxide, 912 grams (11.4 moles). Alkylate, 2580 grams (10.9 moles, basis molecular weight 237). Dry air, 566 liters per hour (45% of mixture).

PROCEDURE. Dry air at 566 liters per hour was admitted to the assembled sulfonator (Figure 3): The liquid sulfur trioxide was next charged to the vaporizer, which was then connected to the sulfonator. The alkylate was measured into the reservoir, after which the rotary pump and homogenizer were started.

The vaporizer was then heated to 46–47° C. with a free flame such that the liquid sulfur trioxide was vaporized over in about 20 minutes. The start of the sulfonation was indicated by a pressure rise in the gas-inlet system, while the end was shown by a corresponding reduction in pressure. The temperature of the reaction mixture gradually rose from room temperature (30° C.) to 60° C., being controlled by the temperature (12° to 27° C.) and circulation rate of the cooling medium in the heat exchanger. The product was then immediately removed and neutralized.

The appearance of the sulfonic acid was the same as for the flask sulfonation. The neutralization procedure was the same, except that drifting to the acid side was not always noted, even with samples from the same batch of alkylate.

Bleaching Procedure. To a 1000-ml. beaker 360 grams of neutralized slurry was charged and heated by external hot water bath to 50° to 60° C. After the pH had been adjusted to about 5 with alkyl sulfonic acid, 10 to 20 grams of 5% sodium hypochlorite was added. Alternate addition of sulfonic acid and bleach was continued until 75 grams of bleaching solution had been added. The final pH was in the 9 to 11 range. Steady agitation was maintained.

Hypochlorite bleaching of aromatic sulfonates is standard industrial practice (*29*).

Product Quality. Using the best commercially available dodecylbenzene alkylate, a product of the following typical slurry analysis can be obtained by the above two procedures.

Unsulfonated oil (active ingredient basis), %	1.5
Sodium sulfate (total solids basis), %	3.2
Active ingredient (total solids basis), %	95.5
Color of slurry (unbleached)	Light cream
Color of slurry (bleached)	Near white

Analyses were made on the slurries by variations (*13*) of standard procedures (*41*, *44*). Water was determined azeotropically using hexane. Sodium sulfate was determined by ethyl alcohol precipitation, and the alcoholic filtrate was extracted with hexane for estimation of unsulfonated oil. The figure for active ingredient was obtained by difference.

Performance tests (Draves test, foaming power, and stability and detergency) showed negligible differences between sodium salts produced from sulfur trioxide and by the standard procedure using 20% oleum. However, the product prepared from sulfur trioxide had an improved odor.

Discussion of Process Variables. The following conclusions

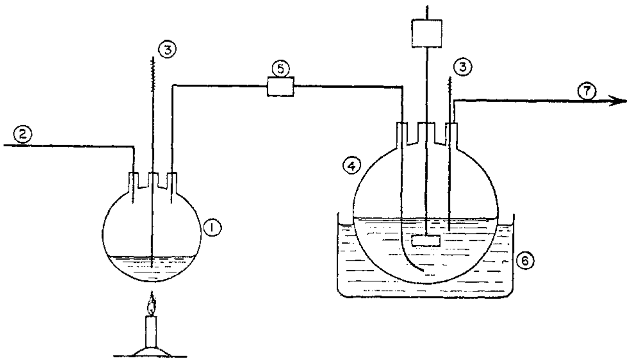

Figure 2. Equipment for Flask Sulfonation

1. Liquid sulfur trioxide vaporizer flask, 250-ml. 3-necked borosilicate glass flask, heated with small burner, equipped with input for metered dry air, thermometer, and gas exit
2. Dry air input
3. Thermometer
4. Reactor flask, 1000-ml. 3-necked borosilicate glass flask, equipped with mechanical paddle agitator, gas input tube with end open and extending to bottom of flask, thermometer, and fume exit
5. Tygon connection
6. Cooling bath
7. Fume exit

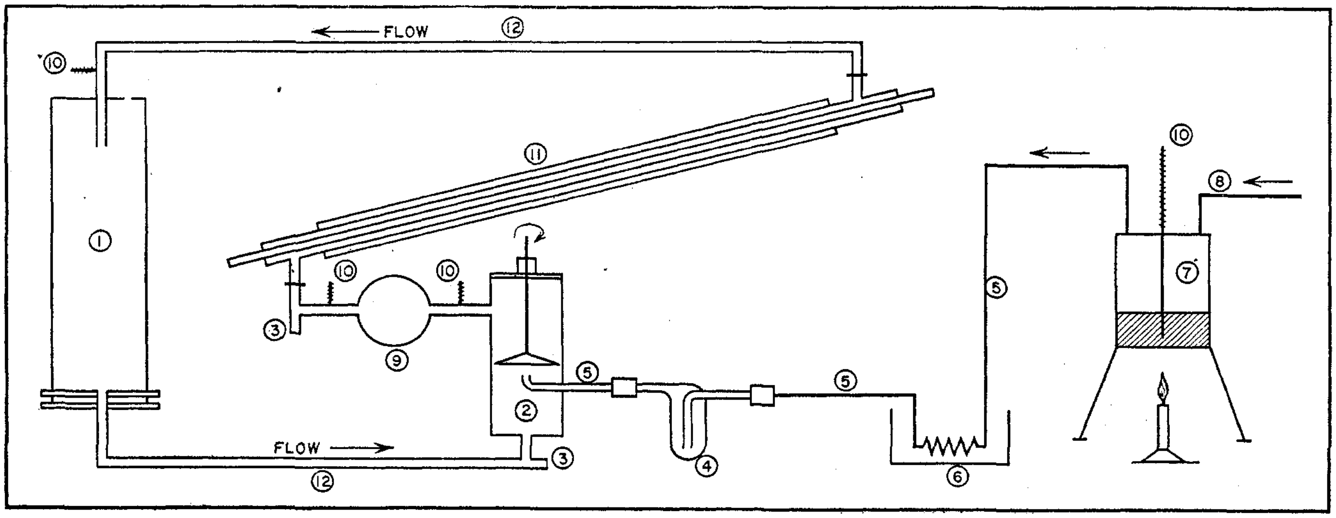

Figure 3. Equipment for Cyclic Sulfonation

1. Reservoir, 4-liter capacity, borosilicate glass piping 4 inches in outside diameter, open or vented at top
2. Homo-mixer, mounted in 2-inch stainless steel pipe as housing (Eppenbach, Inc., 45-10 Vernon Blvd., Long Island City, N. Y.)
3. Drain
4. Visual mist trap, glass, connected to 1/4-inch stainless steel tubing with Tygon tubing
5. Sulfur trioxide vapor-air input line, 1/4-inch stainless steel tubing partially constricted at exit
6. Heat exchanger, 1/4-inch stainless steel coil
7. Liquid sulfur trioxide vaporizer, 4-liter stainless steel kettle direct fired, equipped with thermometer well, inlet for dry metered air, vapor exit line, and bung (not shown) in top for charging liquid sulfur trioxide and cleaning
8. Input line for dry metered air, equipped with pressure gage
9. Circulating pump, rotary pump, Model RI-00, rated capacity 5 gallons per minute at 50 pounds per square inch (Foster Pump Works, 50 Washington St., Brooklyn, N. Y.)
10. Thermometer
11. Concentric tube cooler, for waste or other coolant
12. Piping, 1-inch stainless steel used throughout

were drawn regarding process variables during this study, involving over one hundred laboratory experiments.

ALKYLATE QUALITY. A variety of commercial and semicommercial dodecylbenzene detergent alkylates have been compared in the present process over the past 2 years. Although these products are assumed to be generally similar chemically, considerable variation was noted in the color and free oil content of the slurries obtained. Choice of a good quality alkylate is essential, since changes in process conditions did not compensate for inferior quality in the hydrocarbon.

TABLE IV. COMPARISON OF ALKYLATES FROM VARIOUS SOURCES

Alkylate	Excess SO_3 Used, %	Color[a]	Unsulfonated Oil, %
Neolene 400 (new)	5	Light cream (50)	1.5
Neolene 400 (old)	15	Light tan	2.0
A	15	Dark	6.3
B	15	Dark	4.0
C	15	Dark	3.7
D	5	Light cream (50)	2.2
E	5	Dark (250)	1.7

[a] Figures indicate colors of 10% aqueous solutions as obtained with Klett-Summerson photoelectric colorimeter, test tube model, using No. 42 filter.

The best alkylate tested to date is Neolene 400 (Continental Oil Co., Baltimore, Md.), improved grade available March 1952. This product has a narrower boiling range (535° to 603° F.) (*12*) than previously available alkylates. It was found to yield the best colored slurry, to be more easily sulfonated (only 5% excess sulfonating agent necessary for acceptable free oil content of slurry), and to yield a product of highest active ingredient content (about 95%).

A summary of the data obtained in comparing various alkylates is given in Table IV.

DIGESTION PERIOD. Digestion of the reaction mixture after introduction of the sulfur trioxide is unnecessary for completing the reaction and leads to some increase in color. This is in contrast to the recommended procedure for oleum sulfonation (*52*).

AGITATION. In the flask reactor, increasing the speed of agitation from 200 to 1400 r.p.m. improved slurry color only slightly. This was observed in a series of runs made under the conditions of the typical run cited above at agitation rates of 200, 500, 900, 1300, and 1400 r.p.m. Changing to a creased (Morton) reactor flask from a standard laboratory flask resulted in only slight improvement in color.

With the pump sulfonator, operation of the Homo-mixer reduced the unsulfonated oil content of the final slurry. In a series of four runs made under comparable conditions using 15% excess sulfur trioxide, oil figures of 1.8 and 2.0% were obtained in two cases when operating the Homo-mixer; values of 3.8 and 5.0% were noted in the other two runs made with the mixer not in operation. Color was the same with and without use of the mixer.

METHOD OF INTRODUCTION OF GAS. With the cyclic sulfonator, the gas mixture came in contact with the alkylate at the rotor of the Homo-mixer. Slurry color was the same whether or not the mixer was used; excess sulfonating agent was, however, required to achieve satisfactory free oil content when the mixer was not used. In the flask sulfonation, sensitive alkylates developed most color during the final period of gassing, and considerable improvement resulted from a slowed input rate toward the end. No improvement resulted from use of a fritted-glass dispersion disk; an open-ended tube was used. Sucking back of alkylate into the input tube gave poor color.

REQUIRED EXCESS SULFONATING AGENT. Minimum excess sulfonating agent was used compatible with satisfactory free oil content of the product. The preferred alkylate, in flask sulfonation, showed the following results using varying percentages of excess sulfonating agent:

Excess Used, %	Free Oil, %
0	3.3
5	1.5
10	1.2
15	1.1

It was concluded that, with this alkylate, 5% excess sulfonating agent yielded a product with a satisfactory free oil figure (below 2%). Alkylates previously available required 15% excess sulfonating agent to achieve the same result. Most of the excess sulfur trioxide appears in the slurry as sodium sulfate; smaller percentages appear in the exit gas as unreacted sulfur trioxide and as sulfur dioxide.

NATURE AND PERCENTAGE OF CARRIER GAS. A comparable series of runs was made in the flask reactor, essentially as detailed above for the typical run, except that the percentages of air used in the input gas were as follows: 20, 22, 50, 57, 65, 79, 86, 88, and 90. Some improvement in slurry color was noted at 79% and above. Below this figure, the slurry color remained the same with decreasing percentages of air.

With the cyclic system a somewhat darker slurry was obtained using 1.5% air compared with that obtained with 45% air as in the typical experiment cited above. Nitrogen was found to have no advantage over air as a diluent gas.

SULFONATION TEMPERATURE. Reaction temperature should be kept as low as possible compatible with efficient agitation. In a series of four comparable runs, made in the flask reactor essentially as detailed above in the typical experiment, the reaction temperatures were 45°, 50°, 65°, and 70° C.; only a slight increase in color was noted as the temperature was raised. In other experiments it was found that darkening becomes noticeable at about 70° C. and at 80° C. is substantial with reaction times of about 20 minutes or more. However, brief exposure to as high a temperature as 95° C. is not seriously detrimental, as discussed more fully below.

SULFONATION TIME. Since the reaction is nearly instantaneous, the minimum contact time compatible with heat removal may be used. This is illustrated more fully below.

To explore extreme conditions with respect to the last three process variables, runs were made in the cyclic process with deliberate overloading of cooling capacity. Data for one run are as follows:

Alkylate, 13.0 moles
Liquid sulfur trioxide, 13.65 moles
Time of introduction of sulfur trioxide, 8 minutes
Reaction temperature 20–83° C.
Air in gas, 1.5%
Coolant temperature, 4° C.

Slurry color was somewhat darker than usual, but was easily bleached to near white. Free oil (active ingredient basis) was 3.3%, which is higher than normal.

TABLE V. SULFONATION OF DIAMYLNAPHTHALENE

Weight of hydrocarbon, grams	2850 (11.71 moles)
Weight liquid sulfur trioxide, grams	1080 (13.47 moles)
Diluent air, %	20
Operating temperature, ° C.	Start 60; max. 109; end 100
Operating time, min.	25
Digestion, min.	30 at 90–95° C.

DIAMYLNAPHTHALENE

Sulfonated dialkyl naphthalenes have long been used as industrial wetting agents. The sulfonation step is usually conducted with acid or oleum in large excess (*48*), thereby leading to the formation of a low-active product or spent acid. It therefore seemed of interest to consider the use of sulfur trioxide for this type of sulfonation. Use of sulfur trioxide dissolved in liquid sulfur dioxide has been reported (*5*).

A commercial grade of mixed amylnaphthalenes (Pentalene 95, Sharples Chemicals, Inc.), prepared by Friedel-Crafts alkylation of naphthalene (*30*), was sulfonated in the circulating pump system described above for detergent alkylate sulfonation. Because of the greater viscosity of the sulfonic acid, a higher temperature range was used with the naphthalene compound to obtain good circulation. Details of a run are tabulated in Table V, the indicated digestion period being arbitrary.

The crude sulfonic acid so obtained was converted to the sodium salt and compared, with respect to analysis and performance, with a similar sulfonate prepared by sulfonation of 1000 grams of hydrocarbon with 760 grams of 100% sulfuric acid and 403 grams of 95.5% sulfuric acid, followed by neutralization and benzene extraction. Product analyses, expressed on an anhydrous basis, are reported in Table VI.

TABLE VI. ANALYSIS OF SODIUM DIAMYLNAPHTHALENE SULFONATE

	Sulfonating Agent	
	Sulfur trioxide, %	Sulfuric acid, %
Active sulfonate	85.7	84.7
Inorganic (as Na_2SO_4)	3.6	11.2
Unsulfonated oil	10.7	4.1

TABLE VII. COMPARATIVE PERFORMANCE DATA OF SODIUM DIAMYLNAPHTHALENE SULFONATES

Detergency (by Launderometer, change in reflectance)	Same
Wetting and penetrating power (Draves)	Same
Rewetting (at 0.1, 0.5, and 1.0% concentrations)[a]	Same
Color	Both dark; sulfur trioxide product darker
Solubility	Both gave clear aqueous solutions at 1%
Hard water stability (at 100 p.p.m. hardness)	Sulfur trioxide product clear, acid product somewhat turbid

[a] Procedure of American Association of Textile Chemists and Colorists.

Comparative performance data of the two products are given in Table VII.

Long-Chain Primary Alcohols. Little attention has been given to the possible direct sulfation of alcohols with sulfur trioxide. In fact, it has been stated that, "as sulfur trioxide alone gives side reaction of oxidation or charring with all but a few alcohols, it is rarely used directly as a sulfating agent unless diluted with an inert solvent" (*54*). It has been found in the present study, however, that sulfur trioxide vapor is suitable for the nonsolvent sulfation of lauryl and several other commercially available long-chain, saturated, primary alcohols, the sulfates of which are of practical interest as surface active agents.

Sodium lauryl sulfate has long been manufactured for use as a detergent and wetting agent. Although sulfur trioxide has been mentioned as a possible sulfating agent for this alcohol (*3*), no experimental data have been noted respecting such a process, except for use of the sulfur trioxide–dioxane complex (*55*). Such a process would necessitate recovery and recycle of the dioxane in commercial practice, and therefore has not been considered attractive.

In practice, this sulfation has been conducted with excess sulfuric acid or oleum, or with chlorosulfonic acid (*22*, *47*). The former process yields a product high in sodium sulfate, which may be purchased more cheaply as such rather than by formation in situ. The latter process, while yielding a high-active product, entails disposal of liberated hydrogen chloride, except when operating on a cyclic basis.

TYPICAL LABORATORY PREPARATION. The apparatus and procedure were the same as used for flask sulfonation of the detergent alkylate as described above. Liquid sulfur trioxide (152 grams, 1.9 moles) was vaporized in a stream of dry air (850 liters per hour, yielding a gas of 92% air content), and passed into lauryl alcohol (372.5 grams, 1.9 moles, Du Pont Lorol 5). The reaction temperature was maintained in the 33° to 40° C. range by external cooling with cooled water, care being taken not to freeze the alcohol (melting point 15° to 18° C.) with extreme cooling. The alcohol was vigorously agitated during the reaction period (about 35 minutes). During the initial stage of the reaction, some of the sulfur trioxide passed through unreacted, as lauryl alcohol appeared to be a poor scrubber; however, absorption was excellent after formation of some lauryl sulfate. The reaction mixture was mobile throughout and gave no difficulty with agitation, being much less viscous than the aromatic sulfonic acids at the same temperature.

The crude reaction product weighed 514 grams (loss 10.5

grams), and was tan in color. A portion (408 grams) was neutralized by addition to aqueous caustic soda (800 grams of 7.5% solution), at 20° to 40° C. (Theory for pure lauryl sulfate is 780 grams of 7.5% caustic.) Color of the aqueous sodium salt solution is light yellow, considerably lighter than that of the unneutralized sulfate.

Analysis of a typical product, sodium lauryl sulfate solution, by the analytical procedure cited above for dodecylbenzene sodium sulfate, gave:

Water, %	60.6
Sodium sulfate, %	0.9
Unreacted alcohol, %	1.2

The same sulfation procedure has also been successfully applied to other saturated straight-chain alcohols derived from coconut oil (octyl, decyl, cetyl, and octadecyl), and to C_{10} and C_{13} branched-chain primary alcohols (CPS 224 and 216, Enjay Co., Inc.). In the cases of cetyl and octadecyl alcohols (melting points 45–47° C. and 54° C.), sulfation of the molten alcohols was necessarily run at a higher temperature (70° to 80° C.). If desired, the sodium alkyl sulfate solutions may be bleached with sodium hypochlorite, using the general technique described above for detergent alkylates.

SUBSTITUTION FOR CHLOROSULFONIC ACID

In certain sulfation reactions, as for lauryl and similar saturated primary alcohols, sulfur trioxide can be substituted for chlorosulfonic acid which is commonly used. In the preparation of aromatic sulfonyl chlorides, sulfur trioxide can be partially substituted for chlorosulfonic acid. In both cases, the substitution of sulfur trioxide eliminates the evolution of the equivalent hydrogen chloride formed when chlorosulfonic acid alone is used in the standard procedure. This hydrogen chloride, comprising over 30% of the weight of chlorosulfonic acid, must be purchased, shipped, and disposed of, in addition to being unproductive.

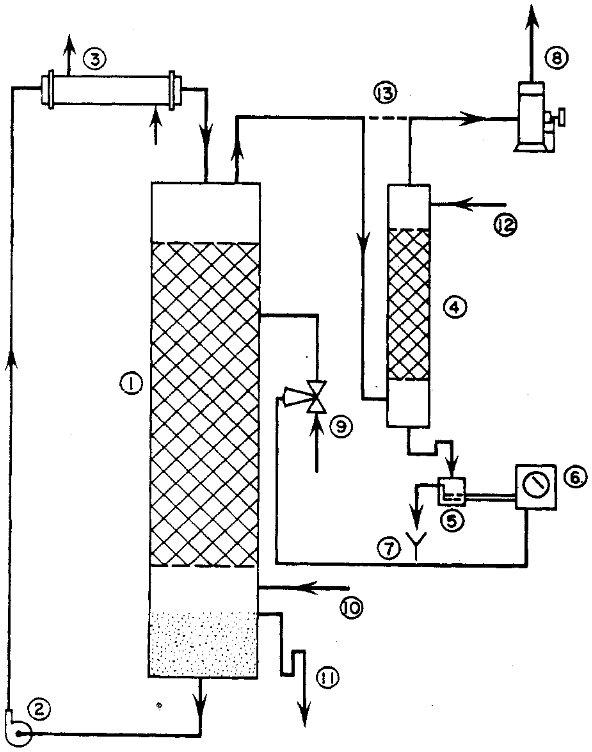

Figure 4. Chlorosulfonic Acid Production Unit

1. Reaction tower, steel, with ceramic packing
2. Circulating pump, stainless steel, Teflon packing, centrifugal type
3. Steel cooler, for use with river water
4. Absorption tower for removal of excess HCl, ceramic, Haveg, or Pyrex
5. Conductivity cell
6. Controller
7. Waste disposal
8. Exhaust fan, rubber-lined steel
9. Liquid sulfur trioxide input
10. HCl gas input
11. Product take-off
12. Water inlet
13. Bypass valves, Stainless steel with Teflon packing

Bypass piping. HCl, Pyrex, porcelain, or Pfaudler

Liquid sulfur trioxide, steel (schedule 80)

Chlorosulfonic acid, steel (schedule 80)

In certain situations, however, it may not be desirable or chemically possible to substitute sulfur trioxide directly for chlorosulfonic acid in the reaction itself. In such cases, the use of an absorption tower for reacting the evolved hydrogen chloride with liquid sulfur trioxide to recreate chlorosulfonic acid appears practical. Thus, chlorosulfonic acid is still used as the chemical reagent, but sulfur trioxide is in effect the sulfonating agent, the evolved hydrogen chloride being recycled. The equations involved, for the case of an alcohol sulfation, are:

$$ROH + ClSO_3H \rightarrow ROSO_3H + HCl$$

$$HCl + SO_3 \rightarrow ClSO_3H$$

$$\text{Over-all:} \quad ROH + SO_3 \rightarrow ROSO_3H$$

Figure 4 is a schematic diagram for the continuous production of chlorosulfonic acid from liquid sulfur trioxide and dry hydrogen chloride. The reaction is conducted in a packed tower precharged with chlorosulfonic acid and heat removal is effected by continuous circulation through an external cooler using river water. A slight excess of hydrogen chloride is used, the required amount approaching the theoretical in actual operation; alternative use of the bypass or the residual hydrogen chloride absorption tower is accordingly possible.

For the production of 100 pounds of chlorosulfonic acid per hour, requiring theoretically 68.7 pounds of liquid sulfur trioxide and 31.3 pounds of hydrogen chloride, it is estimated that a tower 6 × 1.5 feet should be satisfactory, using a circulation rate of 5 gallons per minute. The base of the tower would be maintained at about 40° C., and the cooler, with approximately 20 sq. feet of cooling surface, would have a water input temperature of about 27° C., and a water exit temperature of about 32° C. The heat evolved is calculated at 24,800 B.t.u. per 100 pounds of chlorosulfonic acid formed, using recent data for the respective heats of formation (*46*).

A batch-type operation, using cast iron saturators, has been described (*16*).

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Flame-Stability Studies with Mixed Fuels

HYDROCARBONS, HYDROGEN, AND HYDROGEN SULFIDE

PHILIP F. KURZ

Battelle Memorial Institute, Columbus, Ohio

MUCH research has been done on combustion problems in the past 10 years but there is little information pertaining to the behavior of binary or ternary mixtures of fuels or of fuel-additive mixtures.

Earlier work with additives in this laboratory failed to reveal any substances that accelerated the combustion processes of hydrocarbons (*5*), although inhibiting additives were found. For example, both hydrogen sulfide and hydrogen selenide effectively lowered the flame speed of propane-air mixtures when present in additive proportions of less than 5 volume % of the fuel-additive mixture.

These findings suggested that the fuel which will enhance most economically the combustion of a slow-burning hydrocarbon is a fast-burning hydrocarbon. Accordingly, attention was turned to the study of the combustion characteristics of mixed fuels.

A convenient experimental method for studying the behavior of fuels and fuel mixtures is the observation of flame-stability limits. By the limit of flame stability is meant that velocity at which the flame produced by a given composition of fuel and air can just barely be held on the burner or that composition of the fuel-air mixture which must be supplied to the burner in order to produce a flame that can barely be held at a given burner-jet velocity.

Measurements of flame stability, although not directly applicable, are of significance in assessing the suitability of fuels for use in jet engines and in gas turbines, where the prevention of blowoff or blowout is an essential consideration.

Inasmuch as the studies required comparative measurements on identical burners, a burner suitable for studying both fast-burning fuels and slow-burning fuels was necessary. Such a burner was devised, in which the air and the fuel were kept separated until they were admitted into the combustion chamber. A number of burner designs were tried and, of these, a vortex-type burner was chosen for the experimental work with mixed fuels. This type of burner permits the study of the stability of