NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3560

SPONTANEOUS IGNITION STUDIES RELATING TO LUBRICANTS OF REDUCED FLAMMABILITY

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SUMMARY

Increased interest in the use of diesters as lubricants had suggested a study of the influence of the structure of the alcohol moiety on the spontaneous ignition temperature of a series of dialkyl azelates $(ROOC)_2(CH_2)_7$. The data obtained have been interpreted on the basis of the susceptibility of variously attached hydrogen atoms to oxidative attacks. The vapor pressure of some of the diesters has also been shown to play an important role. Several unexpected results were noted.

The determination of spontaneous ignition temperatures has been extended to a number of representative organic phosphorous esters with predominantly aliphatic structures. Those esters possessing high autoignition temperatures have low molecular weights while those having molecular weights in the lubricant range show poor resistance to spontaneous ignition. One seemingly anomalous case was noted.

Previous reports have been concerned with the outstanding resistance to ignition of hydrogenated polyisobutylene and its behavior as an additive in blends. Determination of the change in spontaneous ignition temperature with composition has been carried out with it in combination with a siloxane and with a phosphonate.

The synthesis of polyisobutylene in the lubricant molecular-weight range has been improved in yield. This synthesis has been accomplished by using the low-boiling cut from a prior preparation as the solvent for the succeeding run. Temperature control was exercised to regulate the degree of polymerization.

INTRODUCTION

In the initial phase of the program (ref. 1) the spontaneous ignition characteristics of approximately 50 organic compounds were investigated with a variety of additives and selected metal surfaces. Observations were made on the effect of structure on ignition. The second part of the program (ref. 2) was concerned with compounds of interest as lubricants. The utility of the crucible apparatus was extended by employing spray injection for the less volatile materials as well as by employing the dropwise procedure. It was found that hydrogenated polyisobutylene showed remarkable resistance to spontaneous ignition. This finding was interpreted on the basis of the large percentage of primary hydrogens contained in such polymers. In the last work a practical method of preparing the polymer was devised and a study of its properties and its behavior in blends was reported (ref. 3).

The present phase has been devoted in part to a further extension of work with hydrogenated polyisobutylene. An improved synthesis has been developed and further blends have been investigated. A fundamental study of the effect of the alcohol group on the spontaneous ignition temperatures of esters has also been made, principally with a series of dialkyl azelates and to a lesser extent on organic phosphorous esters.

This investigation was conducted at the University of Cincinnati under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

APPARATUS AND TEST PROCEDURE

The apparatus used in this investigation has been described in references 1 and 2. It comprised a heated metal block into which a crucible of stainless steel was inserted. Ignition temperatures were observed by adding to the chamber a small measured amount of the fuel either as droplets or as a spray. Spray injection is of the most value with compounds in the lubricant range since it minimizes the vapor-pressure limitations of these less volatile materials. This procedure gave rise to some interesting comparisons with the dropwise-addition procedure.

PRECISION

The precision of the crucible method (sometimes called the static crucible method) of determining spontaneous ignition temperatures depends upon the temperature range of the ignition and upon the viscosity and volatility of the compound. The effects of these variables on the determination have been noted in references 1 and 2. For volatile compounds, the precision of the dropwise procedure is generally within 1° to 2° C for those compounds igniting below 300° C and within 3° to 5° C for those compounds igniting above 300° C. For the less volatile materials, the precision for the spray-injection procedure is only slightly less for a viscosity range of 300 Saybolt Universal seconds at 37.8° C. At higher viscosities (i.e., lower vapor pressures) the present spray apparatus is unsatisfactory.

RESULTS AND DISCUSSION

Spontaneous Ignition Characteristics of a Series of Dialkyl Azelates

Table I summarizes the spontaneous ignition data for a series of dialkyl azelates $(ROOC)_2(CH_2)_7$ obtained by both a dropwise-addition and a spray-injection procedure at two air-flow rates. It should be noted that in the dropwise-addition procedure the esters were effectively added in varying-size charges. In the spray-injection procedure the esters were added as a spray or mist, dispersing the ester in the heated cup and thereby greatly increasing the surface area of the liquid and hence the rate of vaporization. In all cases spray addition effected a lowering of the spontaneous ignition temperature, sometimes as much as 100° C. Before use, the esters were heated at 100° C at a 1- to 2-millimeter pressure for 3 hours to remove volatiles and then treated with activated charcoal. All were colorless mobile liquids except the isotridecyl ester which retained a light straw color.

Previous data from reference 1 have shown that varying the acid grouping of a diester has little effect on spontaneous ignition temperatures (see also ref. 4). Extending the carbon chain from 6 to 10 atoms lowered the spontaneous ignition temperature only 24° C:

Diester[a]	Spontaneous ignition temperature, °C
Bis (1-ethylpropyl) adipate	436
Bis (1-ethylpropyl) azelate	420
Bis (1-ethylpropyl) sebacate	412

[a]Dropwise addition at 125-cm^3/min air flow.

The increase in the unbranched carbon chain does account for the decrease in the spontaneous ignition temperature, but the difference is not so significant as in the homologous series of paraffins, alcohols, or ethers. This finding has been interpreted on the basis that oxidative attack essentially occurs at the ends of a molecule since in a long coiled chain the free ends would be most open to attack. In the case of diesters the carboalkoxy groups also would have a shielding effect on the middle of the molecule. It seems plausible, therefore, that in the case of the diesters most of the attack would occur at the alcohol grouping and that the structure of the alkyl group would be controlling in spontaneous ignition characteristics. In the series studied, this assumption seems justified.

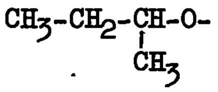
The first member of the series, the dimethyl ester, shows a striking resistance to spontaneous ignition. This observation is in agreement with the work of Boord who pointed out that the relative ease of the substances to oxidative attack may be correlated with the reactivities of their hydrogen atoms, the order of reactivity being tertiary, secondary, and primary in descending order (refs. 5 and 6). The methyl radical has three primary hydrogen atoms making it highly resistant to attack.

On adding methylene groups to the alkyl chain as in the n-propyl and n-butyl, additional less resistant secondary hydrogens come into play; this is evidenced by the progressive drop in spontaneous ignition temperature in both the dropwise and spray additions (the spray technique shows a spread of almost 200° C between the methyl and n-butyl esters).

Comparison of the three butyl esters shows the striking effect of branching. Although the isobutyl and sec-butyl esters have a reactive tertiary hydrogen in the alkyl radical, the number of primary hydrogens has been increased over the n-butyl. The relative values for ease of oxidation as given by Boord are 1:3.6:6.9 for primary to tertiary hydrogens. Summing the contribution of the hydrogens in these radicals gives a value of 24.6 for the n-butyl and 20.1 for the other two. Thus, in the dropwise additions, the spontaneous ignition temperature of the n-butyl ester drops below 400° C, while the other two remain above this temperature. The data obtained by spray injection warrant special attention.

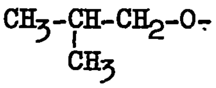
In contrast with the dropwise addition, the spray method substantially reduces the spontaneous ignition temperatures of the n-butyl and isobutyl esters, the latter being even further reduced if cognizance is taken of the appearance of smoke pulses after true flame ignition ceased (the values in parentheses of table I). However, at lower temperatures under these conditions the sec-butyl ester appears much more resistant to ignition. Although smoke pulses were recorded to 280° C for the sec-butyl ester, true flame ignition ceased well above 400° C. It is apparent that some critical factor is operating.

If it is assumed that oxidative attack occurs at the ends of the molecule, it may be considered that the less resistant secondary and tertiary hydrogens in the sec-butyl group are sufficiently protected so that attack must be made at primary hydrogens, which results in a high value. In the case of the isobutyl radical, this shielding effect of the less resistant hydrogens would not be a large factor and a low value might be expected. Another consideration is the effect of the ester linkage:



$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-$

Sec-butoxy



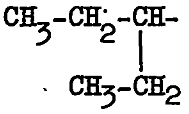
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-O-$

Isobutoxy

The tertiary hydrogen of the sec-butyl is bonded to a carbon adjacent to the strong electronegative atom of oxygen. Ease of free-radical attack by molecular oxygen at this hydrogen conceivably might be reduced. However, in the case of the isobutyl group, the tertiary hydrogen is further removed from the ester linkage and is more susceptible to free-radical attack.

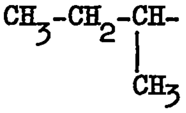
Whatever the case may be, it is apparent from the "smoke pulse" ignitions of the sec-butyl ester, which extend well over a 100° C range, that the tendency to flame ignition is present, and under optimum conditions true flame ignition would probably occur.

Spontaneous ignition by the spray method was observed at temperatures as low as 337° C for the 1-ethylpropyl ester. Comparing this ester with the sec-butyl ester it may be seen that in extending the branched chain by one methylene group, and thus adding two more secondary hydrogens, the spontaneous ignition temperature is greatly reduced:



$CH_3-CH_2-\underset{\displaystyle CH_3-CH_2}{\underset{|}{CH}}-$

1-Ethylpropyl

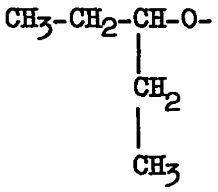


$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$

Sec-butyl

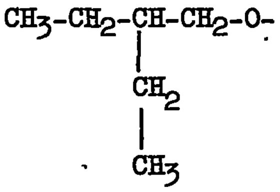
Smoke-pulse ignitions were observed below 300° C, but no minimum temperature could be obtained because of the small quantity of material.

In order to compare it with the 1-ethylpropyl group another methylene has been added in the 2-ethylbutyl group, and the diester shows a further drop in spontaneous ignition (to 264° C by spray injection). In addition, in the 2-ethylbutyl group the tertiary hydrogen is further removed from the effect of the ester oxygen than in the case of the 1-ethylpropyl group and thus may be more susceptible to free-radical attack:



$CH_3-CH_2-\underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{CH}-O-$

1-Ethylpropoxy



$CH_3-CH_2-\underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{CH}-CH_2-O-$

2-Ethylbutoxy

The three octyl esters exhibit approximately the same ignition characteristics. By the spray-injection method the capryl (1 methylheptyl), the 2-ethylhexyl, and the isooctyl esters ignite in the low-temperature region, that is, at less than 300° C (see ref. 7 for a discussion). Likewise, by the dropwise addition, the three esters all ignite within a narrow range of each other by both air-flow rates. At first it might be expected that octyl esters should have lower spontaneous ignition temperatures than those previously considered since additional less resistant secondary hydrogens have been added to the carbon chain, but, comparing them with the 2-ethylbutyl ester, they have higher values by both addition procedures. A possible explanation follows.

The spontaneous ignition is essentially a vapor-phase free-radical process and requires a critical number of activated centers for inflammation to occur. Because of the low vapor pressure of the liquid investigated, this condition cannot be realized, the activated centers being continually dissipated before a critical number can be obtained. In such a case, ignition does not occur. It is possible that this phenomenon is operative with the octyl esters where the spontaneous ignition temperatures are higher than for the 2-ethylbutyl ester because of their lower vapor pressures (using the relative viscosities as a criterion[1]).

This phenomenon becomes even more important in the two highest molecular weight esters investigated where vapor pressure becomes an extremely critical factor, especially with spray injection. Although with this procedure the surface area of the liquid is greatly increased over the dropwise method, thus increasing the amount of vapor at any one time, the low volatility of the isodecyl and isotridecyl esters results in the formation of insufficient activated centers in the low-temperature range. Thus the esters, instead of igniting in the 250° to 300° C range by spray injection, begin to approach the higher range found by the dropwise addition. In the latter procedure the vapor pressure is not so

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[1] Data from a recent private communication have confirmed the assumption that the relative viscosities of the higher molecular weight azelates may be used as a criterion of vapor pressures. Compare the last two columns of table I.

critical a factor since the spontaneous ignition temperatures can be obtained only in the higher range which is approximately that found for the lower azelates.

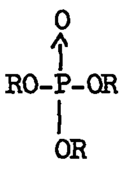
As Scull points out (ref. 8), two of the methods by which aircraft fire hazards can be reduced are by increasing the minimum ignition temperature (the spontaneous ignition temperature) and by lowering the volatility of lubricants. It appears that because of the low volatility of the higher esters the spontaneous ignition temperature is increased. However, as is the case in the paraffins, some leveling-off temperature should be reached as the carbon chains are lengthened.

It should be noted that in all cases of spontaneous ignition temperatures obtained at an air-flow rate of zero cubic centimeters per minute by both the spray-injection and dropwise-addition procedures the values were never lower than those obtained at 125 cubic centimeters per minute. This fact suggests that in the case of the dibasic esters spontaneous ignition is favored by a low fuel-air ratio which is the reverse of the situation that prevails with hydrocarbons, where ignition is favored by a high fuel-air ratio.

Lacquer formation was found to some extent in all the esters investigated. Generally, it was found that the lower the temperature, the greater the formation of lacquer, especially when ignition did not occur. Also the higher the molecular weight of the ester, the greater the formation of lacquer. Below 350° C the octyl esters left appreciable residue. In the case of the isodecyl and isotridecyl esters, even more lacquer formation occurred, the latter also depositing a small amount of carbon. In all cases this deposit could be removed by raising the temperature above 450° C.

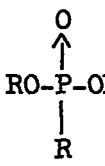
Spontaneous Ignition Characteristics of Some Organic Phosphorous Compounds

The phosphorous compounds investigated consisted of two types, phosphates and phosphonates; the first class may be considered esters of phosphoric acid and the second, esters of an alkyl or aryl phosphorous acid where R may be the same or different:



$$\mathrm{RO{-}}\underset{\underset{\mathrm{OR}}{|}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{{-}OR}$$

Phosphate



$$\mathrm{RO{-}}\underset{\underset{\mathrm{R}}{|}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{{-}OR}$$

Phosphonate

Table II summarizes the spontaneous ignition characteristics of these phosphorous esters with data from other sources.

In all cases except one, data correlate with the postulate that increasing the alkyl chain length and thus adding less resistant secondary hydrogens decreases the stability to oxidative attack. Considering first the phosphates, a general decrease of the spontaneous ignition may be seen in proceeding from the triethyl to the trioctyl phosphate. The triethyl and tributyl phosphates both show outstanding resistance to ignition. In comparing the spray-injection values with those of a diester, such as the di-n-propyl or butyl azelate, this behavior seems surprising since there appear to be ample secondary hydrogens which may act as points of free-radical attack. However, the oxygens of the phosphate group ($\equiv PO_4$) are probably much more effective in resisting free-radical attack on the alkyl chain than is the case with the diesters. In the trihexyl and trioctyl phosphates where the alkyl chain has been increased, this effect seems to be damped, and the spontaneous ignition temperatures are greatly reduced.

The phosphonates studied all show poor ignition characteristics except one doubtful case which is discussed below. The bis (2-ethylhexyl)-2-ethylhexane phosphonate shows low spontaneous ignition temperatures, especially by spray injection. As previously noted (ref. 3), this low ignition region seems to be characteristic of esters containing the 2-ethylhexyl group. The bis (2-ethylhexyl) azelate also showed low values by the spray procedure (approximately 280° C). These results are consistent with the high percentage of less resistant hydrogens of the alkyl group (59 percent).

The dihexyl benzene phosphonate shows the expected results in comparison with the dioctyl ester. It gives slightly higher values which may be interpreted on the basis of a smaller percentage of secondary hydrogens. The benzene group appears to effect partial resistance to ignition since it essentially contains more resistant primary hydrogens. This effect would account for the somewhat higher values ($> 300^\circ$ C) obtained in comparison with other hexyl or octyl esters ($< 300^\circ$ C).

Somewhat higher values are also obtained in the case of the dioctyl isooctene phosphonate where the stability of the olefin radical increases resistance to ignition in contrast with the behavior of the alkyl radicals (see ref. 1). Thus spontaneous ignition temperatures occur above 300° C in the same range as the benzene phosphonates. However, the dinonyl isooctene phosphonate which should fall in this same range showed surprisingly resistant characteristics in agreement with the observation of Dr. Larsen of the Shell Development Co.

As has been the practice, the candidate lubricants were purified only by removing volatiles, which were present in negligible amounts, under reduced pressure. In effect, therefore, the esters were tested as received from the manufacturers. Information from the manufacturer of these phosphonates, the Victor Chemical Works, shows that the dioctyl ester was a distilled product of over 99 percent estimated purity (boiling point, 176° to 178° C at a 1-millimeter pressure), whereas the dinonyl ester was a "bottoms" product of about 94 percent estimated purity. The former may be considered essentially pure, whereas the latter was acid to 0.1N base (0.05 cubic centimeter per 10 grams) and probably contained phosphoric acid. This impurity could very well have acted as an inhibitor giving the unexpectedly high results.[2]

With most of the phosphorous compounds tested, the residue after ignition was quite extensive. The triethyl and tributyl phosphates were relatively volatile and left little residue except a clear lacquer which turned into a white crust. This formation increased as the temperature was lowered from 500° to 250° C and became more apparent when ignition did not occur. The latter also left some carbon at lower temperatures. The trihexyl phosphate deposited appreciable carbon of a powdery appearance especially at lower temperatures. The phosphonates all left a heavy black crustlike deposit as the temperature was reduced. This deposit became so extensive that it sometimes inhibited ignition so that the metal surface had to be cleaned periodically to obtain a minimum value. Generally it was found that the lower the temperature, the greater the residue.

Improved Synthesis of Polyisobutylene

A practical method of synthesis of polyisobutylene has been previously described (ref. 3). By using the low-boiling cut containing isooctane and low polymers from the initial batch run as a diluent and reactant to initiate the next run, an increased yield of 74 percent of polyisobutylene in the desired viscosity range was realized.

Isobutylene gas (Phillips Pure Grade) and catalytic amounts of boron trifluoride were introduced into isooctance as the initial solvent from 0° to 15° C with efficient stirring. The mixture was washed with alkali and then with water until neutral. After drying over potassium

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[2] It has been pointed out that in the two phosphonates considered the octyl radical is 2-ethylhexyl, the nonyl radical is 3,5,5-trimethylhexyl, and the isooctene radical is 2,2,4-trimethylpentenyl. The dinonyl ester then has 12 more primary hydrogens than the dioctyl ester and 6 less secondary hydrogens, a fact which might account for the great difference. Summing up the Boord values for the two esters gives 101.2 for the hydrogens of the dinonyl ester and 118.1 for the hydrogens of the dioctyl ester.

carbonate, the solution was stripped of both isooctane and the low-boiling polymers through triisobutylene by distilling to 100° C at 30- to 40-millimeter pressure. This distillate was used to initiate the next batch run, while the residue was taken as product.

After six consecutive runs in this manner, a yield of 12.5 pounds of polyisobutylene in the desired viscosity range (43 Saybolt Universal seconds at 37.8° C) was obtained. This product is 74 percent of theoretical yield based on the isobutylene (see table III).

Loss of yield occurs from unreacted low polymers and from mechanical loss of isobutylene through supersaturation of the reaction mixture. It was noted during the runs that a more desirable product could be obtained if the temperature during reaction was maintained between 0° and 5° C. Above this temperature range more of the low polymers were obtained as is evident from a comparison of the third and fourth runs with the fifth and sixth.

While maintaining proper temperature control, mechanical loss of isobutylene may be controlled by regulating the ratio of boron trifluoride to isobutylene addition.

Two gallons of polyisobutylene were prepared in accordance with the request of Mr. J. C. Mosteller of the Wright Air Development Center for a gallon of hydrogenated polyisobutylene. Because of inadequate facilities in this laboratory for the hydrogenation of such a quantity, the sample was forwarded to Dr. L. C. Gibbons of the NACA Lewis Flight Propulsion Laboratory for hydrogenation and subsequent fractional distillation.

Spontaneous Ignition Temperatures of Blends With Hydrogenated Polyisobutylene

Polydimethyl siloxane mixtures (spray injection).- The curves for the spontaneous ignition temperature versus composition for mixtures of hydrogenated polyisobutylene (32 Saybolt Universal seconds at 37.8° C) and a siloxane (DC-200 series, 50 centistokes at 25° C) at two air-flow rates are shown in figure 1. They do not show any tendency for inhibition of ignition by the hydrogenated polyisobutylene. It is probable that the lower igniting component, the siloxane, contributes much more to the ignition characteristics of the blends than does the hydrogenated polyisobutylene.

Bis (2-ethylhexyl)-2-ethylhexane phosphonate mixtures (spray injection).- Figure 2 shows the curves for phosphonate-hydrogenated polyisobutylene blends. The easily ignited phosphonate is little inhibited by the hydrogenated polyisobutylene, but there is a characteristic inflection point. As was noted in reference 3, this inflection point lies at about 40 percent by volume hydrogenated polyisobutylene where there is an increase in the spontaneous ignition temperature of the lower igniting component of from 60° to 80° C. Here it amounts to an increase of about 30° C. The curves are similar to those obtained for the bis (2-ethylhexyl) adipate blends (ref. 3, fig. 2).

CONCLUDING REMARKS

Spontaneous ignition temperatures have been determined for a series of dialkyl azelates by two addition procedures at two air-flow rates. It appears that the spontaneous ignition characteristics of a dibasic ester are primarily controlled by the structure of the alcohol moiety of the ester since, in varying the alcohol group, wide variations in these characteristics are obtained. The discussion of such phenomena is consistent with the relative ease of oxidative attack on the particular type of hydrogen atom of the alcohol group. Another contributing factor to the ignition characteristics is the vapor pressure of the ester: The lower the vapor pressure, the more ignition is inhibited.

The spontaneous ignition characteristics of several organic phosphates and phosphonates were obtained. The results are again explained on the basis of the relative ease of oxidative attack of the hydrogen atoms of the alkyl groups. An explanation for the unexpected behavior of one compound is given.

An improved yield for the practical synthesis of polyisobutylene has been developed. This yield amounted to 12.5 pounds of polyisobutylene in the lubricant molecular-weight range (74 percent of theoretical).

The variation in spontaneous ignition temperature with composition has been determined for blends of hydrogenated polyisobutylene with a siloxane and with a phosphonate. Little inhibiting effect by the hydrogenated polyisobutylene was apparent. However, in the latter blend a characteristic inflection point was noted at about 40-percent hydrogenated polyisobutylene content which amounts to about a 30° increase in the spontaneous ignition temperature of the lower igniting component.

University of Cincinnati,
Cincinnati, Ohio, March 15, 1954.

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TABLE I

EFFECT OF ALKYL GROUPS OF AZELAIC DIESTERS $(RCO_2)_2(CH_2)_7$

ON SPONTANEOUS IGNITION TEMPERATURES

Alkyl group (R)	Spontaneous ignition temperature, °C				Number of types of hydrogen			Approximate relative viscosity at 37.8° C, Saybolt Universal sec	Vapor pressure, mm Hg at 400° F
	Spray injection and air flow, cm³/min, of -		Dropwise addition and air flow, cm³/min, of -						
(a)	125	0	125	0	Primary	Secondary	Tertiary		(b)
Methyl CH_3-	438	448	450	456	3	0	0	29	---
n-Propyl $CH_3(CH_2)_2$-	326	326	424	438	3	4	0	35	---
n-Butyl $CH_3(CH_2)_3$-	258	260	384	389	3	6	0	39	---
Isobutyl $(CH_3)_2CHCH_2$-	296 (286)	334 (294)	412	422	6	2	1	40	---
sec-Butyl $CH_3CH_2(CH_3)CH$-	[c]422	[c]432	438	445	6	2	1	39	---
1-Ethylpropyl[d] $CH_3CH_2(C_2H_5)CH$-	[e]337	[e]339	[f]420	---	6	4	1	--	---
2-Ethylbutyl $CH_3CH_2(C_2H_5)CHCH_2$-	264 (260)	264 (260)	379	390	6	6	1	49	4.3
2-Ethylhexyl $CH_3(CH_2)_3(C_2H_5)CHCH_2$-	280 (270)	285 (276)	382	399	6	10	1	65	1.3
1-Methylheptyl $CH_3(CH_2)_5(CH_3)CH$-	272 (263)	272 (263)	398	406	6	10	1	67	1.4
Isooctyl[g]	289 (268)	290 (268)	395	400	8	7	2	69	1.1
Isodecyl[g]	313	329	392	402	10	8	3	100	.5
Isotridecyl[g]	362	382	396	398	13	11	3	184	.1

[a] Obtained from Emery Industries, Inc., Cincinnati, Ohio, except where otherwise noted.

[b] Used through courtesy of Esso Research and Engineering Co.

[c] Smoke pulse obtained down to 280° C.

[d] Obtained from U. S. Naval Research Laboratory, Washington, D. C.

[e] Smoke pulse obtained below 300° C but no minimum.

[f] From reference 1.

[g] The alcohols from which the iso-groups are derived are mixtures having mono- and dimethyl-branched chains in the ratio of about 1 to 3. The number of types of hydrogens has been approximated on this basis.

TABLE II

SPONTANEOUS IGNITION TEMPERATURES OF SOME ORGANIC PHOSPHOROUS COMPOUNDS

Compound and source	Spray injection, cm^3/min		Dropwise addition, cm^3/min	
	125	0	125	0
Triethyl phosphate (Tennessee Eastman Co.)	484	488	488	488
Tributyl phosphate (Commercial Solvents Corp.)	472	473	476	474
Trihexyl phosphate (Victor Chemical Works)	286	287	291	293
Trioctyl phosphate (Shell Development Co., ONR N-9-37501)	---	---	---	285
Bis (2-ethylhexyl) - 2-ethylhexane phosphonate (Virginia-Carolina Chemical Corp.)	267	275	342	368
Dihexyl benzene phosphonate (Victor Chemical Works)	320	320	326	322
Dioctyl benzene phosphonate[a] (Victor Chemical Works)	316	316	314	315
Dioctyl isooctene[a] phosphonate (Victor Chemical Works)	329	330	320	319
Dinonyl isooctene[b] phosphonate (Victor Chemical Works)	455	465	444	452

[a] From reference 3.

[b] See remarks in section "Results and Discussion."

TABLE III

PREPARATION OF POLYISOBUTYLENE

Run	Relative viscosity at 37.8° C, Saybolt Universal sec (a)	n_{25}^{D}	Reaction temperature, °C
1	40	1.4511	5 to 12
2	48	1.4527	5 to 12
3	31	1.4473	5 to 15
4	32	1.4485	5 to 15
5	56	1.4542	0 to 8
6	72	1.4559	0 to 5
Total	43	1.4516	------

[a] After stripping up to 110° C at a pressure of 30 to 40 mm to remove low-boiling polymers up through triisobutylene.

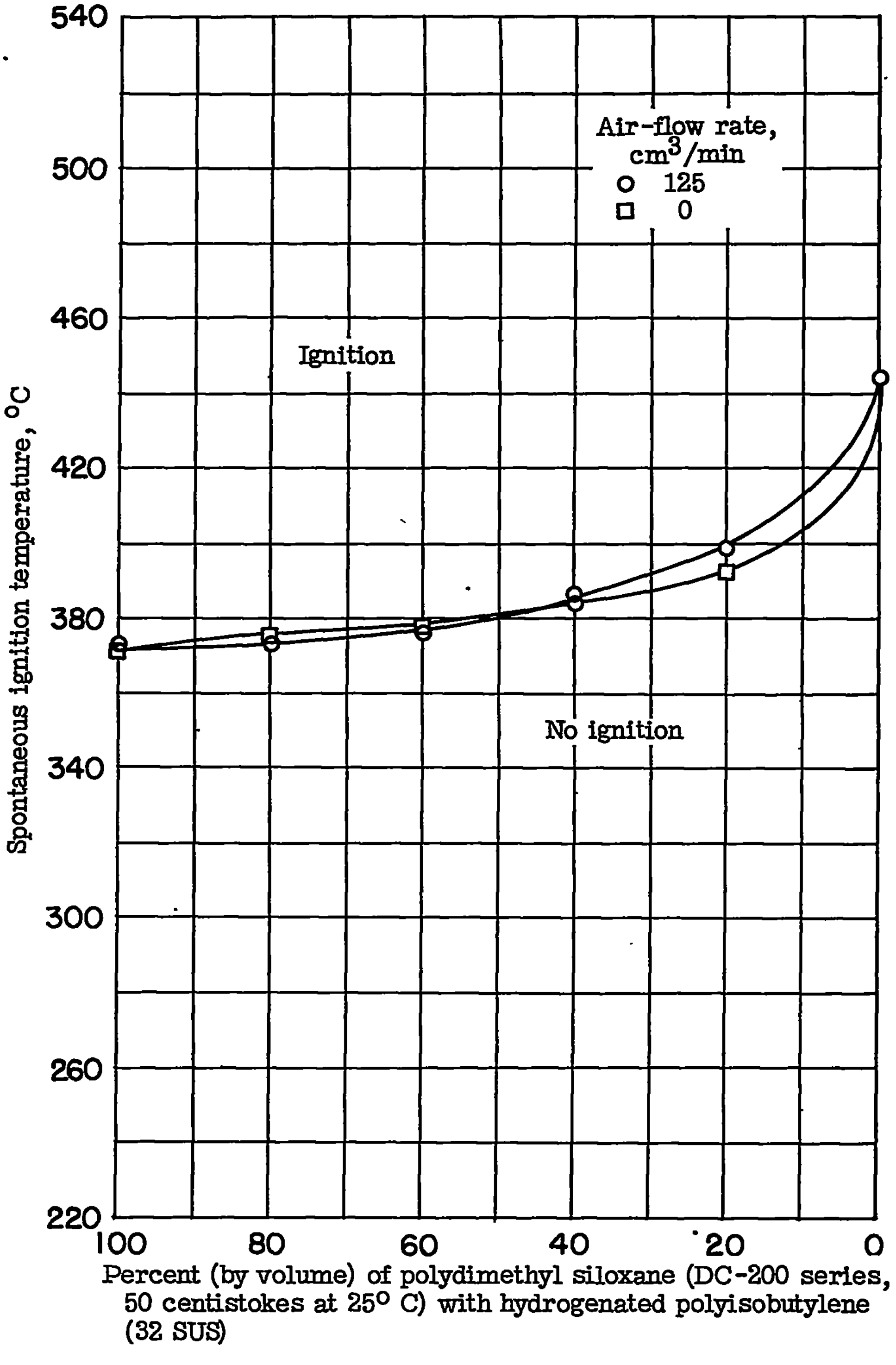

Figure 1.- Spontaneous ignition characteristics of various polydimethyl siloxane-hydrogenated polyisobutylene mixtures. Stainless-steel cup assembly; spray-injection procedure. 32 Saybolt Universal seconds.

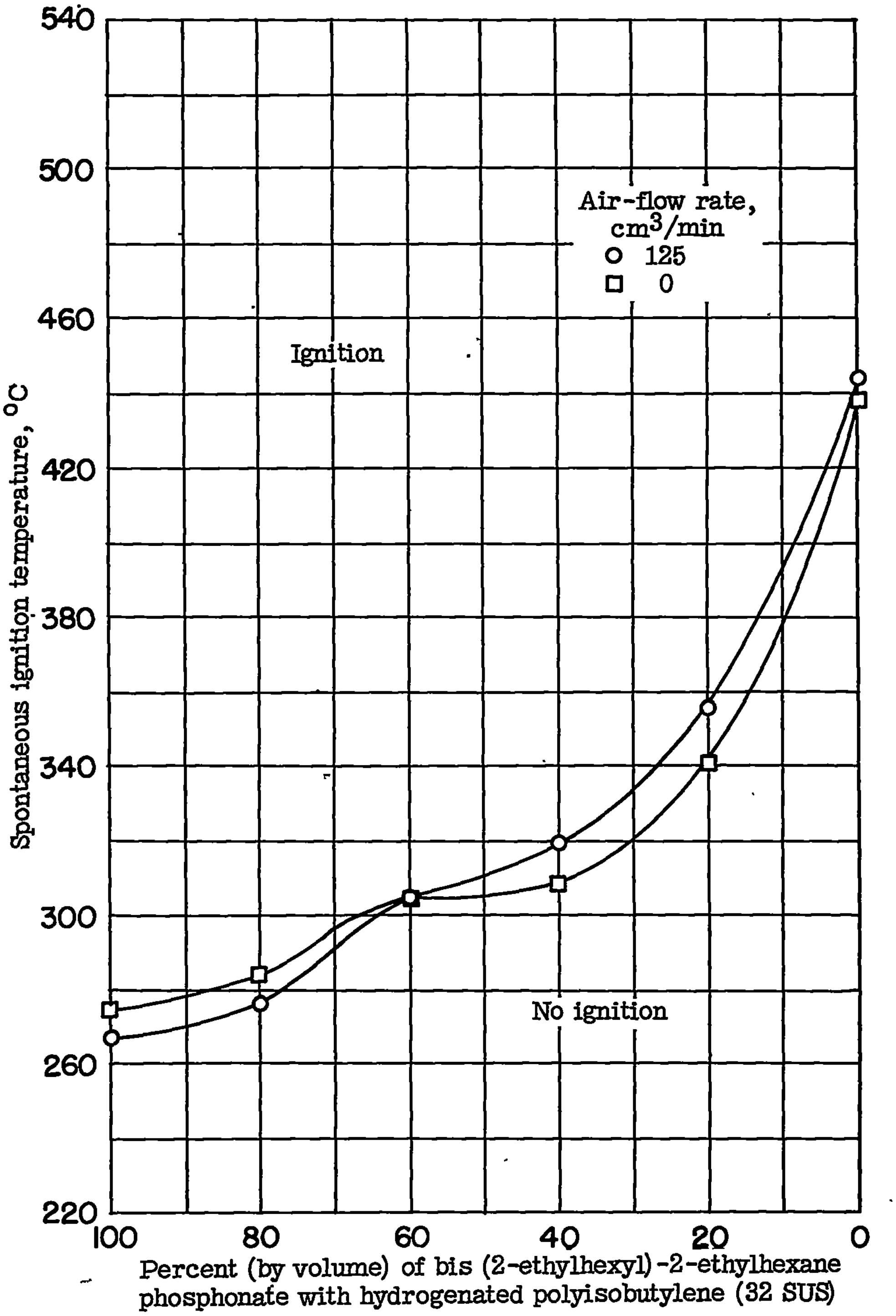

Figure 2.- Spontaneous ignition characteristics of various bis (2-ethylhexyl)-2-ethylhexane phosphonate-hydrogenated polyisobutylene mixtures. Stainless-steel cup assembly; spray-injection procedure.

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