-9 MAR. 1960

$A99$/F. R. Note No. 418

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

THE EFFECT OF VARIOUS POWDERED MATERIALS ON THE STABILITY

OF PROTEIN FOAMS

by

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Summary

The effect of some powders on the stability of foam has been examined both in fire tests and a small-scale laboratory test developed by the U.S. Naval Research Laboratory. The results of these test methods are compared.

Some materials which would probably cause little foam breakdown in practice are suggested.

January 1960

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Table 1

Composition of powders

Powder identification	Material	Specific surface cm^2/gm.
Proprietary powders		
A	Sodium bicarbonate with 3 per cent talc and 1.5 per cent magnesium stearate	3,990
B	Sodium bicarbonate with 5 per cent calcium hydroxyphosphate	1,100
C *(Foam compatible)*	Sodium bicarbonate with 2 per cent talc and 2 to 2.5 per cent proprietary high melting point wax	1,370
D *	Potassium sulphate with 8 per cent mica and 0.2 per cent magnesium stearate	3,350
Non-proprietary powders		
E	Sodium bicarbonate with 0.2 per cent magnesium stearate	1,050
F	Cement with 0.2 per cent magnesium stearate	3,340
G	Cement with 1.5 per cent magnesium stearate	3,730
H	Sodium borate (Borax) with 0.2 per cent magnesium stearate	1,240
J	Ammonium carbonate with 0.2 per cent magnesium stearate	$< 1,000$

* This is the subject of patent applications.

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Introduction

The use of dry powder extinguishing agents in conjunction with mechanical foam is likely to occur during fire fighting operations against aircraft crash fires [1]. Previous work [2], in which two sodium bicarbonate-based powders were investigated, has shown, however, that serious breakdown of mechanical foam can be caused by some dry chemical extinguishing agents, especially those containing a metallic stearate.

In view of the increasing interest in foam-compatible powders, the work was extended to develop a laboratory test for assessing compatibility and to examine the desirable properties of powders to give compatibility with protein foams. The two fire tests which were used in the earlier investigation [2] and which are detailed briefly below, were considered to represent adequately, the worst condition likely in the combined operational use of powder and foam. The results of any small scale laboratory tests on powders should be capable of correlation with their performance on the fire tests. To establish this correlation, nine different types of powder were subjected to both the fire test and the most promising of the two laboratory tests investigated. A wider range of powders was then examined using the laboratory test. Although these investigations are not complete, it was felt that the results already obtained should be recorded, as they are likely to affect the future development of this type of dry powder.

Correlation of fire tests and laboratory test results - Dry powders used.

The performance of nine different types of powder has so far been investigated on the fire tests and their composition is given in Table 1. Two of these (A and B) are standard dry powder extinguishing agents used in the previous work [2] and two are proprietary powders stated to be 'foam compatible'. The remainder of the powders were ground and mixed in the laboratory.

Fire tests

The test fire was made in a steel tray 3 ft in diameter and 4 in. deep, containing a $1\frac{1}{2}$ in. depth of petrol. After ignition, the petrol was allowed to burn for one minute before the application of powder or foam. A laboratory foam generator was used to produce foam of expansion 7 and critical shearing stress 500 dyne/cm^2 ± 10 per cent from a 3 per cent solution of a protein-based compound. Some tests were carried out with a more fluid foam of critical shearing stress 200 dyne/cm^2 ± 10 per cent. A nozzle, placed 8 ft from the centre of the fire and 4 ft above the petrol surface, directed foam into the centre of the burning petrol. Complete extinction was not possible by this method of application since the foam became contaminated with petrol.

Three radiometers, placed around the fire, were used to measure the radiant intensity. As in the previous experiments [2] the 'control' time was taken as the time to reduce the intensity of the fire to 15 per cent of its initial value.

Two fire test methods were used.

Method 1. The effect of the prior application of dry chemical on the critical rate of application of foam

The 'critical' rate of application of foam may be defined as the rate below which 'control' of a fire is impossible.

Foam was applied to the fire at a steady rate and the 'control' time measured. Tests were made at different rates of application and a graph of 'control' time against rate was plotted, the rate asymptote of this curve giving the 'critical' rate.

Similar tests were made in which a known quantity of powder was sprayed into the tray before the application of foam. Where possible the powder was applied in such a way that the fire was reduced but not extinguished. When the application of powder had ceased, the fire was allowed to regain its initial intensity, and foam was then applied.

The 'critical' rates of foam application with four of the powders tested were determined.

Method 2. The effect on the stability of a foam layer of the application of dry chemical to its surface

Foam was applied to the fire at a rate of 0.14 gal/ft^2/min (7 times the critical rate of application). The application of foam was continued after 'control' until a further $1\frac{1}{4}$ gal. of foaming liquid had been applied. The time for the intensity of the residual fire to rise to one-third of the initial intensity was taken as a measure of the stability of the foam layer.

Tests were then made in which the residual fire was extinguished by a known quantity of powder to the surface of the foam. The petrol contained in the foam was then re-ignited and the stability of the foam measured.

Laboratory tests

(a) Conical flask test

The results of the previous investigations [2] on sodium bicarbonate-based powders had suggested that the metallic stearate additive was the main cause of foam breakdown. The stearate is slightly soluble in petrol and it was suggested that it was dispersed by the petrol as it contaminated the foam. It was felt, therefore, that a satisfactory laboratory test could be evolved by measuring the stability of foam which had been passed through petrol containing a sample of the powder under investigation. The final form of the test consisted of a conical flask containing 1 gm. of the powder under test in 100 ml. of petrol through which foam of fixed characteristics was injected. The ratio of the rate of drainage with no powder present to that when a sample of powder was introduced into the petrol was taken as a measure of compatibility.

The results given by this test were consistent with those of the fire tests when sodium bicarbonate-based powders were used. However, powder (D) which caused little foam breakdown in the fire tests and which consisted mainly of potassium sulphate, appeared on this test to behave similarly to sodium bicarbonate containing the same amount of additive. It appears that this test procedure is sensitive to the metallic stearate content irrespective of the chemical composition of the powder whereas in the fire test the chemical composition of the powder also affects foam stability.

(b) N. R. L. Laboratory Test

Details of this test are given in a paper by Jablonski and Gipe [3] who used it to compare sodium bicarbonate-based powders. A preliminary investigation using powder D (potassium sulphate-based) and powder C (sodium bicarbonate-based) showed a reasonable correlation with the fire test results and it was decided to investigate this test in more detail.

The test consists of measuring the rate of drainage from a pan of foam which is irradiated and onto the surface of which 10 ± 0.1 gm. of powder have been applied. Jablonski and Gipe made the foam by using an electric kitchen mixer to give a 25 per cent drainage time greater than 25 minutes. To investigate the suitability of the test for powders of different chemical composition it was felt that a closer control of foam properties was desirable and the foam was therefore made in a laboratory foam generator. In this test foam of expansion 11 and with a critical shearing stress of 750 dynes/cm^2 (25 per cent drainage time about 40 minutes) made from a 3 per cent solution of foam compound was used. The two fire tests classify the powders in the same order and since the burn-back test can be made much more quickly and simply the other five powders were tested in this way.

(c) Comparison of fire test and laboratory test results

The results for the nine powders on the 'burn-back' test and the N. R. L. laboratory test are given in Table 2. The N. R. L. test ratio 'R' is the ratio of the rate of drainage of liquid from the foam with powder on its surface, to the rate of drainage in the control tests, with no powder present.

Table 2

Comparison of laboratory and fire test results

Powder identification	Material	Burn back time		N.R.L. test ratio R	$1/R$
		shear stress 500 dynes/cm²	shear stress 200 dynes/cm²		
A	Sodium bicarbonate with 3 per cent talc and 1.5 per cent magnesium stearate	2.5	1.9	14.0	0.071
B	Sodium bicarbonate with 1 per cent calcium hydroxy-phosphate	9.4	6.4	3.1	0.323
C	Sodium bicarbonate with 2 per cent talc and 2 to 2.5 per cent high melting point wax.	3.4	1.9	5.7	0.175
D	Potassium sulphate with 8 per cent mica and 0.2 per cent magnesium stearate	15.0	5.3	1.0	1.000
E	Sodium bicarbonate with 0.2 per cent magnesium stearate	3.0	1.7	16.0	0.063
F	Cement with 0.2 per cent magnesium stearate	11.8	7.9	1.6	0.625
G	Cement with 1.5 per cent magnesium stearate	5.2ᴹ	-	1.4	0.714
H	Sodium borate (borax) with 0.2 per cent magnesium stearate	5.7	-	23.0	0.043
J	Ammonium carbonate with 0.2 per cent magnesium stearate	9.4	-	5.7	0.175

Note: The results given are the means of at least two tests except for ᴹ which is the result of a single test.

Results

(a) Fire test results

So far four powders have been examined on both the fire tests (Methods 1 and 2), and the results are shown in Figures 1 and 2. Examination of Fig. 2 shows that amounts of powder greater than 0.177 lb/ft² (1.25 lb. total) cause little further reduction in the burn back time and the remainder of the powders were examined with only this quantity of powder applied.

A comparison of the performance of the four powders on the two fire tests is shown by Table 3 and Figure 3.

<p style="text-align:center;"><u>Table 3</u></p>

<p style="text-align:center;"><u>Fire test results</u> (Proprietary powders)</p>

Powder identif-ication	Material	Specific surface cm²/gm.	Crit. rate gal/ft²/min.	Burn back time - min.	
				shear stress 500 dynes/cm²	shear stress 200 dynes/cm²
No powder	-	-	0.02	19.9	11.1
A	Sodium bicarbonate with 3 per cent talc and 1.5 per cent magnesium stearate	3,990	0.45	2.5	1.9
B	Sodium bicarbonate with 1 per cent calcium hydroxyphosphate	1,100	0.05	9.4	6.4
C	Sodium bicarbonate with 2 per cent talc and 2 to 2.5 per cent proprietary high melting point wax	1,370	0.45	3.4	1.9
D	Potassium sulphate with 8 per cent mica and 0.2 per cent magnesium stearate	3,350	0.03	15.0	5.3

There is a linear relationship between the reciprocal of the N. R. L. test ratio and the burn back time in the fire test (Fig. 4). The equation of the regression line for foams of critical shear of 500 dynes/cm^2 is

$$y = 12.2x + 3.42 \qquad \ldots\ldots\ldots(1)$$

where y = burn back time in minutes

x = $^1/R$

R = Ratio: $\dfrac{\text{rate of drainage with powder in ml/min}}{\text{control rate of drainage in ml/min}}$

Discussion

Although there is a considerable scatter of the points in Fig. 4, the test gives a good indication of the degree of compatibility of powders with foam.

Foams of low critical shear stress give lower burn-back times than those of higher critical shear stress, as would be expected. The ratio of 'burn-back' time to 'burn-back' time in the control tests for the foams of high and low critical shear stress are, however, reasonably consistent.

The test results suggest that the degree of foam breakdown due to the metallic stearate additive is dependent on the base powder to which it is added. Materials such as cement ammonium carbonate and potassium sulphate (F. J. and D) containing about 0.2 per cent magnesium stearate cause considerably less severe breakdown than sodium bicarbonate and sodium borate (E and H) containing the same amount of additive.

Jablonski and Gipe in their investigations found that foam made from one type of foam compound was destroyed much more rapidly by sodium bicarbonate than other types tested. Measurements were made of the pH of solution drained from the foam and they concluded that this foam compound was particularly sensitive to variations in pH . In view of this, pH measurements were taken of the liquid drained in the tests with the nine powders investigated. Generally, the liquid collected during tests in which a high rate of drainage occurred, had a high pH value. A probable explanation of this is that powders which cause only slight breakdown are supported on the surface of the foam for the duration of the test so that they do not come into contact with much of the liquid in the foam.

It is known that the stability of protein foams is affected by variations of pH but their stability is also affected by some metallic salts which may themselves produce pH changes. This point is illustrated by further tests which are described in the next section.

Further laboratory tests

(a) Effect of salt solutions on stability of foam

When the powder is in contact with the liquid in the foam, saturated solutions of the salts are likely to occur locally and to give some indication of the effects of these saturated solutions on the stability of different types of protein foam compound, the following procedure was used. Foam was made by an electric kitchen mixer from a foam solution made up with either distilled water or near-saturated solutions of the following salts –

Sodium bicarbonate
Potassium sulphate
Sodium chloride.

The foam compound concentration and mixing time were adjusted with each compound so that when the solution was made with distilled water, foam of expansion between 10 and 11.5 and critical shearing stress of about 750 dynes/cm^2 was obtained. The same concentration and mixing times were then used for the foaming solutions made with the near-saturated salt solutions and the critical shearing stress of the foam measured. It has been shown that the critical shearing stress is a good measure of foam stability [4]. The results of these tests are shown in Table 4.

Sodium bicarbonate causes a considerable reduction in the stability of the foam produced, potassium sulphate increases the stability with all but one of the compounds and when the foam is made with a saturated solution of sodium chloride, the critical shear stress is increased by a factor between 2 and 3. This suggests that if the base salt of a dry powder plays an important role in compatibility, sodium chloride would be a promising powder to investigate.

The marked difference in the effect on the stability with different types of foam compound, suggests that tests on both the laboratory and fire test should be made with a number of different compounds.

(b) Further tests on N. R. L. Laboratory test

Five powders containing varying amounts of magnesium stearate, were mixed in the laboratory. Sodium chloride was chosen as one of these powders as the previous tests had indicated that it might form a suitable base for a compatible powder and it is known to be as effective as sodium bicarbonate as an extinguishing agent [5]. Potassium bicarbonate was also included as a recent report [6] has suggested that it has considerable advantages as an extinguishing agent. The results of these tests are given in Table 5.

Table 5

The effect of magnesium stearate additive on the N.R.L. test ratio

Material	Specific surface cm^2/gm.	N. R. L. test ratio 'R'		
		Quantity of magnesium stearate		
		None	0.2 per cent	1.5 per cent
Sodium bicarbonate	1,050.0	2.4	16.0	14.0
Sodium carbonate	1,100	6.0	23.4	-
Sodium chloride	1,870	1.0	0.8[x]	1.3[x]
Potassium bicarbonate	2,650	8.5	29.4	-
Potassium sulphate	540	1.3	1.5	6.8

[x] These tests were made with foam produced in an electric kitchen mixer as proposed by Jablonski and Gipe [3].

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The criterion suggested [3] for the acceptance of a powder as compatible with foam is that the rate of drainage with powder present should not be more than twice that of the control test (R $\leqslant$ 2). This is approximately equivalent to the powder causing an increase in the critical rate of application from 0.02 gal/ft^2/min to 0.04 gal/ft^2/min on the fire test (Method 1) or reducing the burn-back time (Method 2) from about 20 minutes to 10 minutes. It would certainly seem that powders causing any degree of foam breakdown greater than this should not be accepted.

On this criterion only potassium sulphate and sodium chloride of the salts listed in Table 5 would be acceptable, and it appears that as much as $1\frac{1}{2}$ per cent of magnesium stearate can be included with sodium chloride without appreciably affecting its compatibility. This is a rather surprising result, considering the known foam-breaking properties of the metallic stearates, and it is proposed to investigate this on the fire test.

It is interesting to note that a considerable reduction in the amount of magnesium stearate in the commonly used sodium bicarbonate powder does not appear to render it more foam compatible.

The results of the tests with potassium bicarbonate are at variance with those reported by Jablonski and Gipe [3]. It was thought that these might be due to the different methods of foam production used and tests were made in which foam of similar physical properties was produced by both the laboratory foam generator and the kitchen mixer. The results are given below –

| | N. R. L. test ratio R | | |
Powder	foam from generator	foam from kitchen mixer	Remarks
Potassium bicarbonate (no additive)	8.5	12.4	Means significantly different.
Sodium bicarbonate (no additive)	2.4	2.7	Means not significantly different.

These results suggest that it is only at the higher rates of drainage that there is a significant difference between the two methods of foam production and in the important region of values of 'R' of 2 either method of foam production can be used.

Conclusions

1. The results of the N. R. L. test have been shown to correlate with fire test results for nine powders of different composition.

2. Reducing the quantity of magnesium stearate additive in sodium bicarbonate to 0.2 per cent does not render it more compatible with foam.

3. Both potassium sulphate and sodium chloride appear to be good bases for compatible powders. Up to 0.2 per cent of magnesium stearate can be added to potassium sulphate and probably considerably more to sodium chloride to improve flow and storage properties without sacrificing compatibility.

Acknowledgments

References

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Table 4

Effect of salt solutions on foam stability

Compound No.	Type of foam compound	Critical shear stress - dyne/cm^2			
		Distilled water solution	Sodium bicarbonate solution (near saturated)	Potassium sulphate solution (near saturated)	Sodium chloride solution (near saturated)
1	Hydrolised keratin, stabilised with ferrous sulphate	750	140	840	1,950
2	Solubilised protein, stabilised with zinc and iron salts	750	90	960	1,920
3	A compound from which the stabilising salts have been removed	460	250	640	1,490
4	Hydrolised protein, stabilised with with ferrous and aluminium sulphates	750	160	640	2,020
5	Hydrolised blood, stabilised with ferrous salts	750	300	850	1,850
6	American Compound 'A'	750	340	1,070	1,310
7	American Compound 'B'	750	460	1,170	1,780

+ 8 gm. of Sodium bicarbonate per 100 ml. of distilled water at approximately 20°C.

x 9.2 gm. of Potassium sulphate " " " " " " " "

x 33.3 gm. of Sodium chloride " " " " " " " "

It was not possible to obtain foam with a higher critical shearing stress than 460 dynes/cm^2 when the solution was made with distilled water.
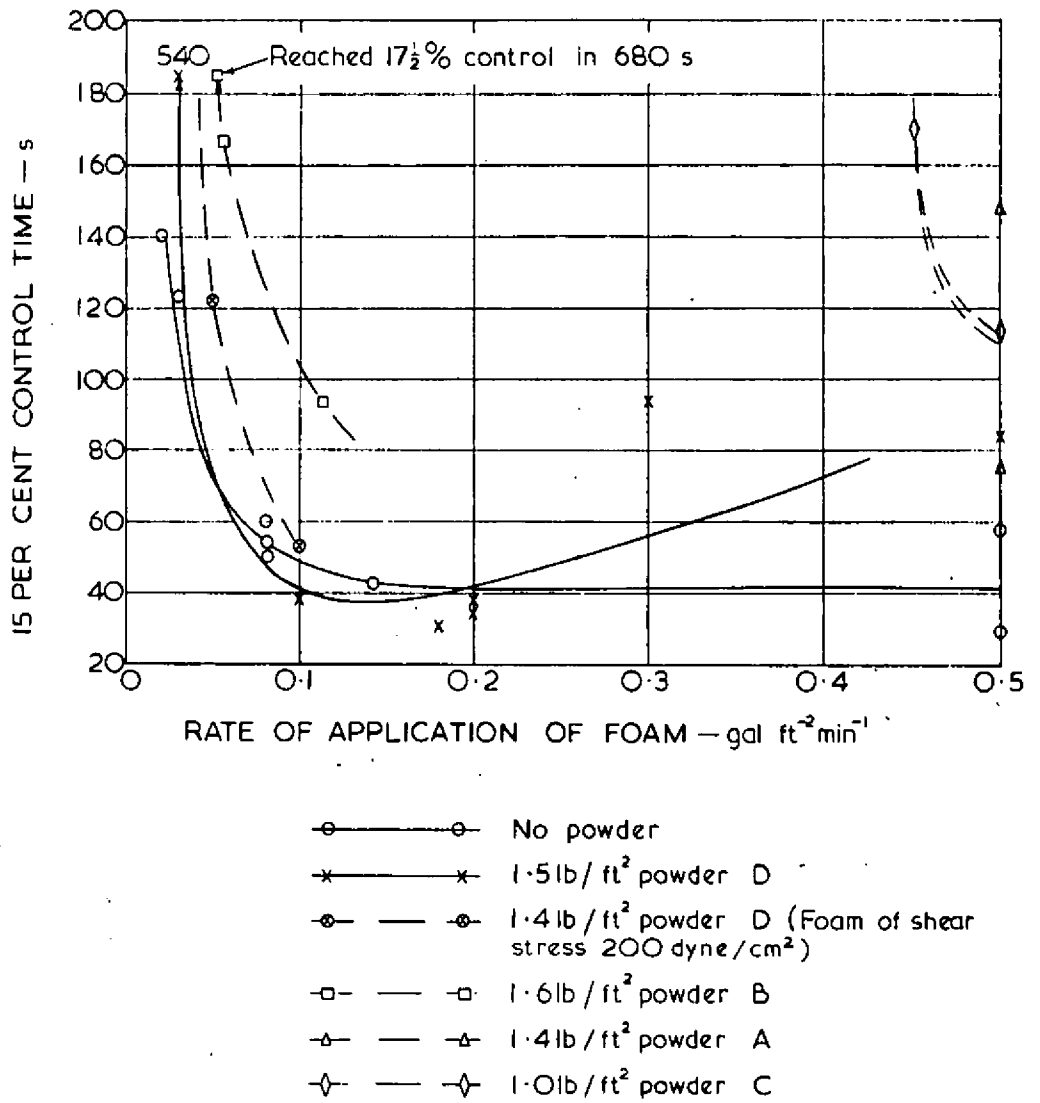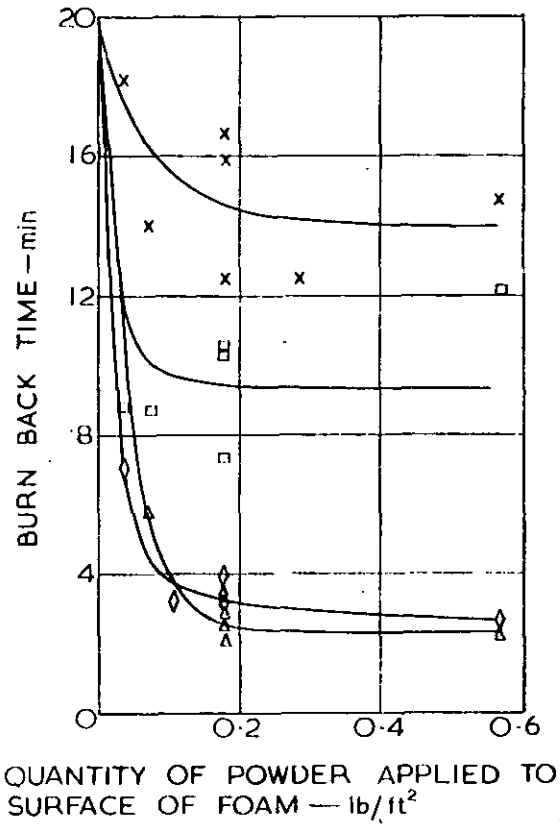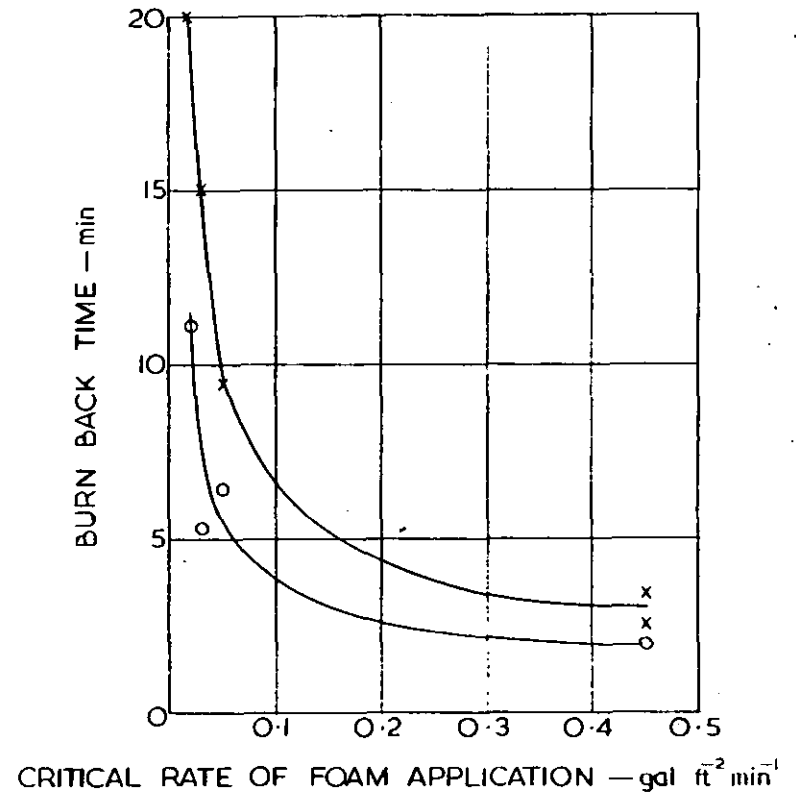
FIG.1. THE EFFECT OF POWDER ON THE CONTROL OF FIRE BY FOAM

QUANTITY OF POWDER APPLIED TO
SURFACE OF FOAM — lb/ft²

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×——× Powder D
▫——▫ Powder B
▲——▲ Powder A
◆——◆ Powder C
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FIG. 2. THE EFFECT ON THE STABILITY OF FOAM
OF THE APPLICATION OF POWDER TO
ITS SURFACE

CRITICAL RATE OF FOAM APPLICATION — gal ft⁻² min⁻¹

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×——× High shear
θ——θ Low shear
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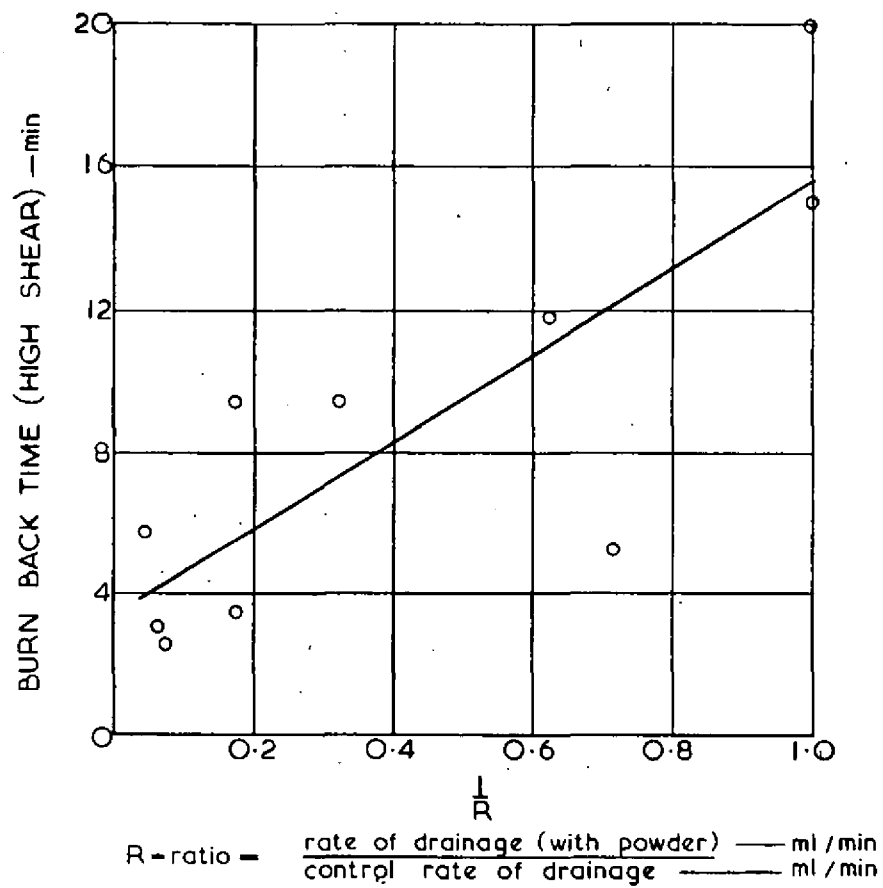FIG. 3. COMPARISON OF THE TWO TYPES
OF FIRE TEST WITH PROPRIETARY
POWDERS

FIG. 4. RELATIONSHIP BETWEEN THE BURN BACK TIME AND THE RECIPRICAL OF THE N.R.L. TEST RATIO