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SOME TESTS ON BORIC OXIDE

by

P. F. THORNE AND D. M. TUCKER

April 1968.

**FIRE
RESEARCH
STATION**

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SUMMARY

Some difficulty has been experienced with boric oxide powder for use on metal fires due to moisture adsorption and caking when stored in extinguishers. A series of experiments has been conducted on boric oxide powder samples of different particle size containing various amounts of flow additives, in order to investigate their moisture absorption and caking characteristics and fire performance.

It was found that both the rate of moisture absorption and the crushing strength decreased with an increase in particle size and, to a lesser degree, with an increase in flow additive. Fire tests showed that the powder was more likely to form a coherent molten film if the stearate content was low and the particle size large. In view of these results it would appear that the optimum powder would have a larger overall particle size than that used at present, and would contain a maximum of 1 per cent stearate. This powder could conveniently be commercial grade boric oxide ground with 1 per cent magnesium stearate for only as long as required for coating the particles.

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SOME TESTS ON BORIC OXIDE

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1. Introduction

Boric oxide (B_2O_3) has been developed for use as a dry powder fire extinguishing agent for metal fires⁽¹⁾⁽²⁾, and is currently being produced to a Ministry of Public Building and Works specification⁽³⁾. Details of the patent and MPBW specifications are given in Appendix I. Difficulty has been experienced with this powder due to moisture absorption and caking, and an investigation has been made into the effects of different amounts of flow additive and the "fineness" of the powder on some powder properties.

The powder samples used in the experiments, full details of which are given in Appendix 2, are summarised below.

- A. A proprietary powder manufactured to the MPBW specification but containing in addition two per cent by weight of calcium silicate.
- B. A powder prepared according to the MPBW specification.
- C. A lightly ground powder containing one per cent magnesium stearate.
- D. As C. above but containing two per cent magnesium stearate.
- E. As C. above but having all material smaller than 170 mesh (90) removed.
- F. As E. above but containing 0.5 per cent magnesium stearate.
- G. Unground and untreated "Technical Grade" powder as supplied.
- H. Untreated "Technical Grade" powder milled until 99 per cent passed a 72 mesh sieve.

The following experiments were performed on the powders.

- 1. Determination of the time required to grind Technical Grade powder containing one per cent magnesium stearate to conform to the MPBW specification in a laboratory ball mill.
- 2. Size analysis (selected sieve and specific surface).
- 3. Measurement of the rate of moisture absorption.
- 4. Measurement of crushing strength.
- 5. Discharge tests.
- 6. Small scale fire tests.

Powders A. to F. were used in all the experiments, powder G. was used in experiments 3 and 6 and powder H. in experiment 3.

2. Experimental

2.1. Powder preparation and comminution experiment.

Powders C. and D. were prepared by mixing the appropriate quantities of boric oxide and magnesium stearate in a laboratory ball mill for 30 minutes. This time produced satisfactory coating with the minimum amount of grinding.

Powder B. was prepared by grinding in the same mill until substantially all the product passed a 72 mesh (210 μ) sieve. The mill was 29.5 cm diameter, 22 cm long, filled to half its volume with 2.5 cm diameter pebbles. The powder to be ground filled the pores between the pebbles and covered them to a depth of $\frac{1}{4}$ inch. The speed of rotation was 56 rpm. At intervals samples were withdrawn, analysed by sieving and returned to the mill. The change in sieve analysis with time is shown in Table 1 and plotted in Fig. 1. The time required to produce powder B. in this equipment was 4 hours.

2.2. Size analysis and apparent density.

Sieve analyses were performed according to B.S. 1796 (1952) using the following meshes 52, 60 and 72 on the "1 per cent stearate powder" and on the "Ministry of Works" powder during preparation as described above. In addition, the "Specific Surface" of all samples was determined using the method of Lea and Nurse⁽⁵⁾. The apparent densities were measured according to DEF 1420 Appendix D. The results of these analyses are given in Table 2 and the sieve analyses plotted in Fig. 2.

2.3. Rate of moisture absorption.

Curves of moisture absorbed against time were determined for the powders using the method developed by Forward⁽⁴⁾. The method consists of suspending powder samples of known weight in shallow pans from sensitive calibrated silica springs in a transparent chamber, the temperature and relative humidity of which are maintained at constant values. The temperature was maintained at $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ by means of a thermostatically controlled water bath and the relative humidity was maintained at this temperature at a constant value of about 92 per cent by means of beakers of saturated sodium carbonate solution, placed at the bottom of the chamber. By means of a travelling microscope, the extension of the springs due to the increase in weight of the samples was measured, and the percentage increase in sample weight due to moisture absorption was calculated. The original weight of powder in all cases was 2.000 ± 0.001 gms. The results are given in Tables, 3, 4 and 5 and plotted in Figs. 3 and 4.

An interesting feature of this experiment was that as moisture was absorbed, the powder beds expanded. Although it was not possible to measure this expansion accurately, the finer powders expanded to about three times their original volume whereas the coarser, unground powders only expanded to about twice the original volume.

2.4. Crushing strength.

The crushing strengths of the four powders were determined according to the procedure laid down in DEF 1420, Appendix C. It was found that, because of the large amounts of moisture absorbed by boric oxide, it was possible to overload a dessicator by placing too many pellets in it. Initially, because of overloading, crushing strengths were found to be extremely high (of the order of 1400 gf) the pellets being characterised by a solid core at the central base which had not dried completely in the specified time. The results given in Table 2 were obtained by reducing the dessicator loading to about half the usual value. It is conceivable that much lower crushing strengths could be recorded by treating single pellets in dessicators of high drying capacity. This is obviously an important factor and should be investigated further. These considerations may also apply to the humidifying chamber.

2.5. Discharge tests

Powders A. and C. were tested for discharge characteristics according to the discharge test specified in DEF 1420. A standard Ministry of Works extinguisher body of nominal capacity 25 lb was filled with powder and discharged. The results are summarized in Table 6.

2.6. Fire tests

(a) Small heaps of powder were heated from above by means of a small blow-torch flame and the following observations made:

(1) Powder A. The surface of the heap first charred then melted but a coherent molten film would not form on the remaining powder. The molten powder contained a number of small bubbles.

(2) Powder B. Charring again occurred and bubbles formed in a sticky mass of half-molten particles.

(3) Powder C. Charring and bubble formation were observed. The bubbles ruptured and although a continuous coherent molten film was not formed, this powder produced a better film than powder A. or B.

(4) Powder D. Both charring and bubble formation and rupture occurred to a greater extent than with powder C. A coherent molten film could not be formed.

(5) Powder G. This formed a clear coherent glassy film with no charring and no bubble formation. Fusion occurred more quickly and more of the powder heap was involved than with the other powders.

(b) Small scale fire tests were then made using approximately 40 gm pieces of magnesium/aluminium alloy. The alloy was heated by means of a blow torch and the molten metal was contained in a shallow depression formed in an asbestos slab. The metal was heated until it was well alight and then left to burn for 10 seconds. Powder was then applied by sprinkling from above and the weight of powder required to extinguish the fire noted. In all cases, combustion of the metal was extinguished in 5 to 10 seconds although the molten metal was still hot enough at this stage for re-ignition to occur if the powder layer was broken. The following observations were made:

(1) Powder A. Weight of alloy 43.5 gms. Weight of powder used 38 gms. The powder formed a "caked" mass over the fire area rather than a completely fused layer. This mass cracked on cooling and when cold a brittle porous solid layer was found next to the metal and most of the remaining powder could be scraped away.

(2) Powder B. Weight of alloy 41 gms. Weight of powder used 48 gms. Charring occurred in the centre of the fire area and small flames licked over the surface. Several small outbreaks occurred at the edges of the fire and after $1\frac{1}{2}$ minutes a patch in the centre became red hot. The powder again formed a "caked" mass as above with a glutinous layer next to the metal which when cool was porous and brittle.

(3) Powder C. Weight of alloy 38.5 gms. Weight of powder 41 gms. In this fire, the molten metal covered an area approximately $1\frac{1}{2}$ times as large as the other fires. The powder again formed a "caked" mass above a glutinous layer, which was found to be porous and brittle when cold. The fire broke through and re-ignited in four places after about 45 seconds, and these outbreaks burnt for a further 30 seconds.

(4) Powder D. Weight of alloy 40 gms. Weight of powder used 60 gms. This powder had the same effect as recorded above. Cracks appeared in the centre of the fire area and this was followed by several minor outbreaks.

(5) Powder G. Weight of alloy 37.5 gms. Weight of powder used 35 gms. The powder readily formed a continuous, glowing layer without flaming or charring. The fire broke through at a thin spot in the layer and the film retreated from the outbreak. When this small incipient fire went out after one minute the film did not flow back over this spot.

3. Discussion

Although the ball mill was loaded (see Section 2.1.) in a way designed to produce optimum grinding conditions, the time taken to produce a given amount of comminution was considerably longer than for other fire-fighting powders. Fig. 1 shows that after 4 hours grinding there was still 0.5 per cent by weight above the maximum size specified in MW/CS/447/1. This was considered to be a sufficient enough compliance with the specification. If this specification is to be rigidly adhered to, however, there will be a point at which it is uneconomic to grind any further. At this stage, which will depend upon the type of mill used, the product should be screened on a 72 mesh sieve and the oversize material recycled to the mill. During grinding, all sizes of particles are being comminuted and whilst grinding is prolonged to eliminate all particles above a given size, the "mean" size is being continually reduced, producing a powder which is undesirably fine, as this investigation suggests.

The results of the grinding analyses are shown again in Fig. 2 together with analyses of the other powders. The proprietary powder tested contained 3 per cent above the maximum specified size of 210 . Details of specific surface are given in Table 2. It is interesting to note that the specific surface of the proprietary powder is over 50 per cent greater than that of the powder prepared to the MPBW specification even though the sieve analyses indicate that the proprietary powder is the coarser, at least in the top size range. It can be shown that

$$\text{Specific Surface} = K \frac{f_i}{d_i} \text{ cm}^2/\text{gm}$$

when K is a constant depending on the powder

f_i is the weight fraction of the powder consisting of particles of diameter d_i .

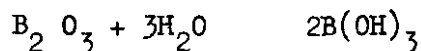
From this equation it can be seen that the addition of a small proportion of very fine material can substantially increase the specific surface of an otherwise predominantly coarse powder. The addition of 2 per cent "Tufnit" (finely divided calcium silicate) could have this effect on the proprietary powder. The specific surfaces of powders C. and D. reflect the stearate contents but not to such a marked degree.

The results of the moisture absorption experiment (Fig. 3) show some interesting features. For the first six hours exposure, the finer powders (A. and B) absorb similar amounts of moisture. Thereafter the powder A. absorbs less moisture than powder B. and behaves rather more like the coarser powders (C. and D). Powder B. absorbs significantly more moisture than the other three powders (A. C or D). There is little to choose between the other powders (A. C. or D) but the order of increasing moisture absorption is consistently D, C, A, except towards the end of the experiment when powder C. absorbs the most moisture of the four.

Powders G. and H. absorbed the most moisture during the time the tests were run. The finer of the two absorbed the most moisture. It can be seen that the addition of 1 per cent magnesium stearate to the fine powder (i.e. powder B) more than compensated for the milling.

The third moisture absorption experiment (Fig. 4) showed that removing the fine fractions of a powder decreased the moisture absorption rate. However, it is difficult to see why powder F. should absorb moisture at a slower rate than powder E.

Boric oxide is hydrated by water to boric acid the reaction being



and the heat of reaction

$$H = -42.0 \text{ k cal/mole at } 25^\circ\text{C}$$

This large heat of reaction results in a vigorous reaction with water. In fact, if boric oxide is mixed with an equal weight of water, the temperature will reach 100°C in about 15 seconds.

The water required to drive this reaction to its theoretical completion is 77.5 per cent by weight of the original boric oxide. It can be seen in Fig. 3 that all powders tend towards this limit after long exposure. On examining the samples after exposure it was found that although some agglomeration had occurred especially with the finer powders, none of the powders was cohesive. This was probably due to the fact that the samples had not been compressed and were free to expand. The reason for the

expansion is not known but could be due to a certain amount of expansion of the crystal lattice necessary to incorporate the water vapour molecules.

The caking test showed the dessicator loading is an important factor when applying this test to boric oxide powders. This factor should be further investigated before such a test is incorporated into any revised MPBW specification.

The crushing strengths of the coarse powders C. and D. were the lowest, the addition of 2 per cent stearate being more beneficial than 1 per cent. Both the finer powders as tested would have failed the MPBW specification, as it stands at present.

Table 6 shows that powder A. passed the discharge test. The coarser powder C. failed to meet the requirement of DEF 1420 that 90 per cent of the contents should be discharged in less than 25 secs. This test was designed for foam-compatible powders, and it may well be that it is not suitable for metal fire powders. Indeed it seems likely that more efficient extinction could be achieved under some conditions by applying the powder in a rather more gentle manner than that designed for flammable liquid fires.

A more appropriate extinguisher for boric oxide would give a low velocity, high density discharge. It would have a long discharge tube which would enable the operation to manoeuvre the nozzle close to the fire for the most efficient application without the need to approach close to the fire.

The small scale fire tests showed first of all that the decomposition products of the stearate resulted in a modification of the surface tension of the molten boric oxide. This prevented a coherent and continuous molten film from being formed readily. On the other hand, the melt containing no stearate flowed too easily, especially away from fresh outbreaks of combustion. All the powders extinguished the fires satisfactorily. Of the treated powders, powders A, C. were marginally better than the others. Although the alloy remained molten beneath the powder layer for up to a minute after powder application ceased, it was found possible to spray water onto the fire area almost immediately without causing explosion or serious reignition of the metal. Normally the application of water would intensify the combustion with a possibility of explosion.

4. Conclusions

(1) It would appear that the best "all round" powder would be a fairly coarse (Technical grade) powder ground with 1 per cent magnesium stearate for just as long as was required for coating the particles, i.e. powder C. This powder would be substantially coarser than the present MPBW specification.

(2) A further advantage would be obtained by sieving out the finer particles (170 mesh), but the advantage would need to be weighed against the increased cost which would be at least 15 per cent.

(3) A modified extinguisher with a low velocity high density discharge through an applicator, and adequate moisture sealing during storage, would be the best method of dispersing powders by hand onto a metal fire.

5. References

- (1) ELKINS, G.H.J. Fire Research Note 545 (March 1964).
- (2) U.K. Patent Application 49358/63.
- (3) MPBW Specification MW/CS/447/1 (1965).
- (4) FORWARD, R. M. F. E. Note 488 (1961) Part 2.
- (5) BS.12 (1958) Portland Cement.

Table 1

Grinding time, hours	Percentage by weight, undersize		
	300 52 mesh	250 60 mesh	210 72 mesh
0	86.4	75.4	62.3
$\frac{1}{2}$	94.2	86.7	74.0
$1\frac{1}{2}$	98.8	96.2	89.4
$2\frac{1}{2}$	99.8	99.1	96.8
3	99.92	99.62	98.24
$3\frac{1}{2}$	99.98	99.8	99.1
4	99.98	99.86	99.52

Progress of Grinding with Time

Table 2
Results of powder analyses

Powder	Percentage by weight undersize			Specific surface cm ² /gm	Apparent (bulk) density gms/cm ³	Crushing strength gmf
	300 52 mesh	250 60 mesh	210 72 mesh			
G	86.4	75.4	62.3	-	-	-
C	94.2	86.7	74.0	830	0.95	66
D	not measured but similar to 1 per cent Mg St.			850	0.94	45
B	99.98	99.86	99.52	1300	0.87	505
A	99.9	99.4	97.2	2030	0.90	810

Table 3

Percentage increase of weight of the powder samples
during the Water Absorption Test

Time (hours)	Cumulative percentage increase in Wt			
	A	B	C	D
1.0	3.0	2.8	2.4	2.1
2.1	4.8	5.1	3.2	3.7
3.5	6.5	7.0	4.8	4.9
5.75	8.0	9.1	5.9	6.0
7.5	9.8	10.8	8.6	8.3
24.5	24.0	30.4	23.0	22.5
26.2	25.0	32.0	24.8	23.7
28.0	26.5	33.6	25.5	24.6
31.0	28.5	35.7	27.3	25.8
48.2	39.2	49.0	39.0	37.2
50.2	40.0	50.8	40.5	39.1
52.2	41.5	52.0	41.5	41.2
72.0	53.5	64.3	51.4	49.8
75.5	54.7	65.5	53.7	52.2
78.7	56.4	66.9	54.8	53.0
143.3	70.8	73.8	74.8	70.4

Table 4

Time (Hours)	Cumulative percentage increase in weight	
	G	H
0.2	1.7	2.0
1.7	5.2	6.1
3.1	7.6	8.8
5.0	9.6	11.0
6.5	11.5	12.8

Table 5

Time (hours)	Cumulative percentage increase in weight		
	F	E	C
0.3	0.7	1.4	1.4
1.9	3.4	3.8	4.4
3.3	4.1	4.6	5.5
5.3	5.1	5.7	6.8
7.3	6.9	7.4	9.2
23.1	16.5	18.0	20.8
25.1	17.3	19.3	22.3
27.5	18.8	20.4	23.8
29.4	20.1	21.4	25.4
30.8	20.4	21.5	25.5
47.2	29.4	31.5	35.7
50.1	30.9	32.8	37.2
51.8	31.7	33.7	37.7
54.1	32.8	34.9	39.3
54.8	33.0	34.9	39.4
73.4	42.0	44.1	48.2
75.8	43.4	45.2	49.2
Total weight increase by direct measurement (gms)	0.8690	0.9005	0.9842
Percentage increase	43.4 per cent	45.0 per cent	49.2 per cent

Table 6

Results of Discharge Tests from 25 lb extinguishers

Powder	Weight of powder charge (lb)	Discharge time (secs)	Percentage of powder discharged
A	24.6	17.0	92.9
C {	24.9	16.0	82.0
	24.6	15.0	85.3

DEF 1420 (Foam Compatible Dry Powder) requires that 90 per cent of the contents be discharged in less than 25 secs.

Appendix 1

	Particle size	Flow additives	Crushing strength when determined according to DEF 1420
Patent specification	"Convenient range of sizes would be 10 - 500 ."	Not less than 1 per cent by weight	-
Ministry of Works specification MW/CS/447/1	All below 210 (72 BS mesh)	0.8 per cent - 1.2 per cent by weight of magnesium stearate	Not more than 150 gf
Specification of raw material (Technical grade B_2O_3 from Borax Consolidated)	100 per cent below 500 (30 BS mesh) 81 per cent below 250 (60 BS mesh) 70 per cent below 210 (72 BS mesh)	-	-

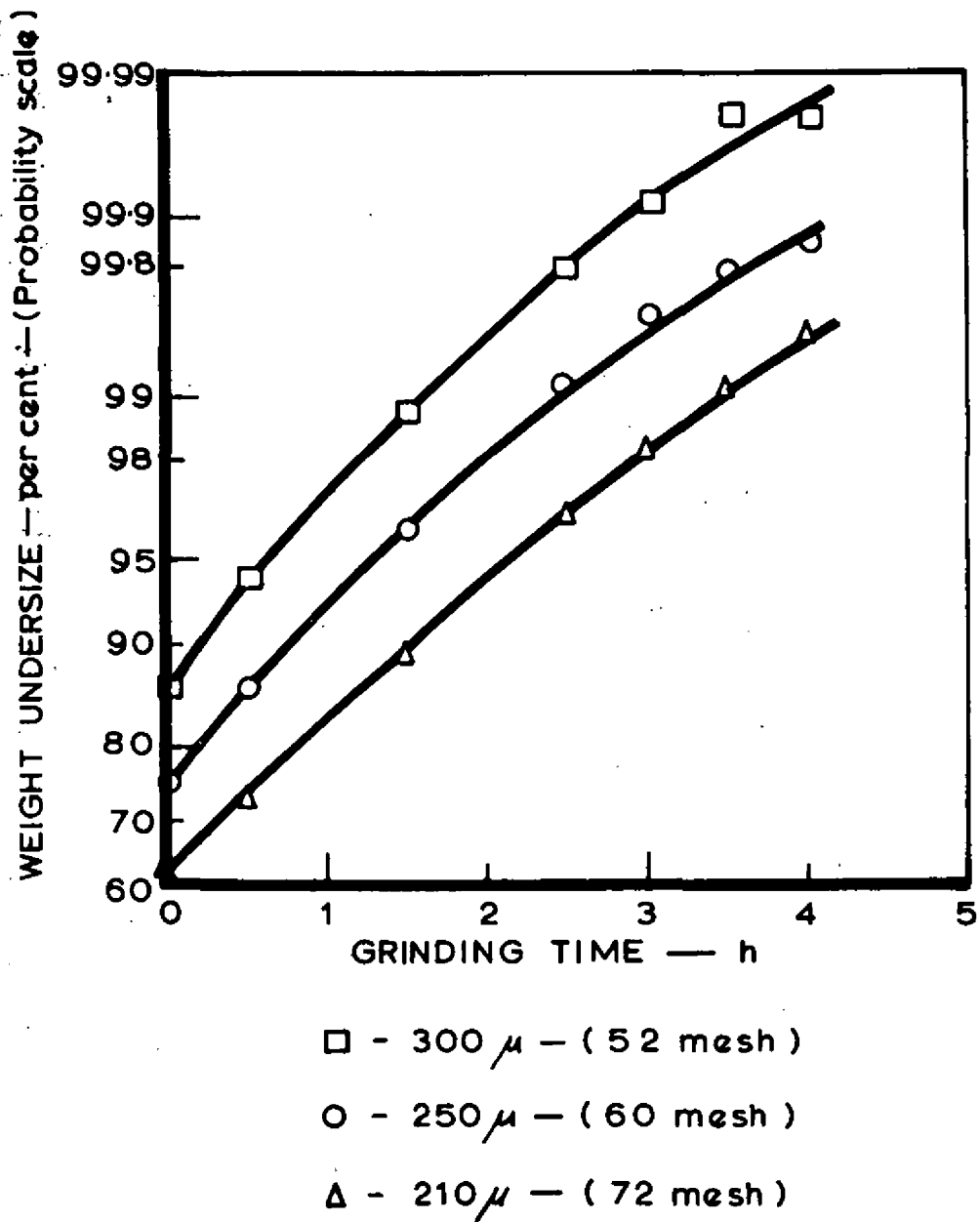
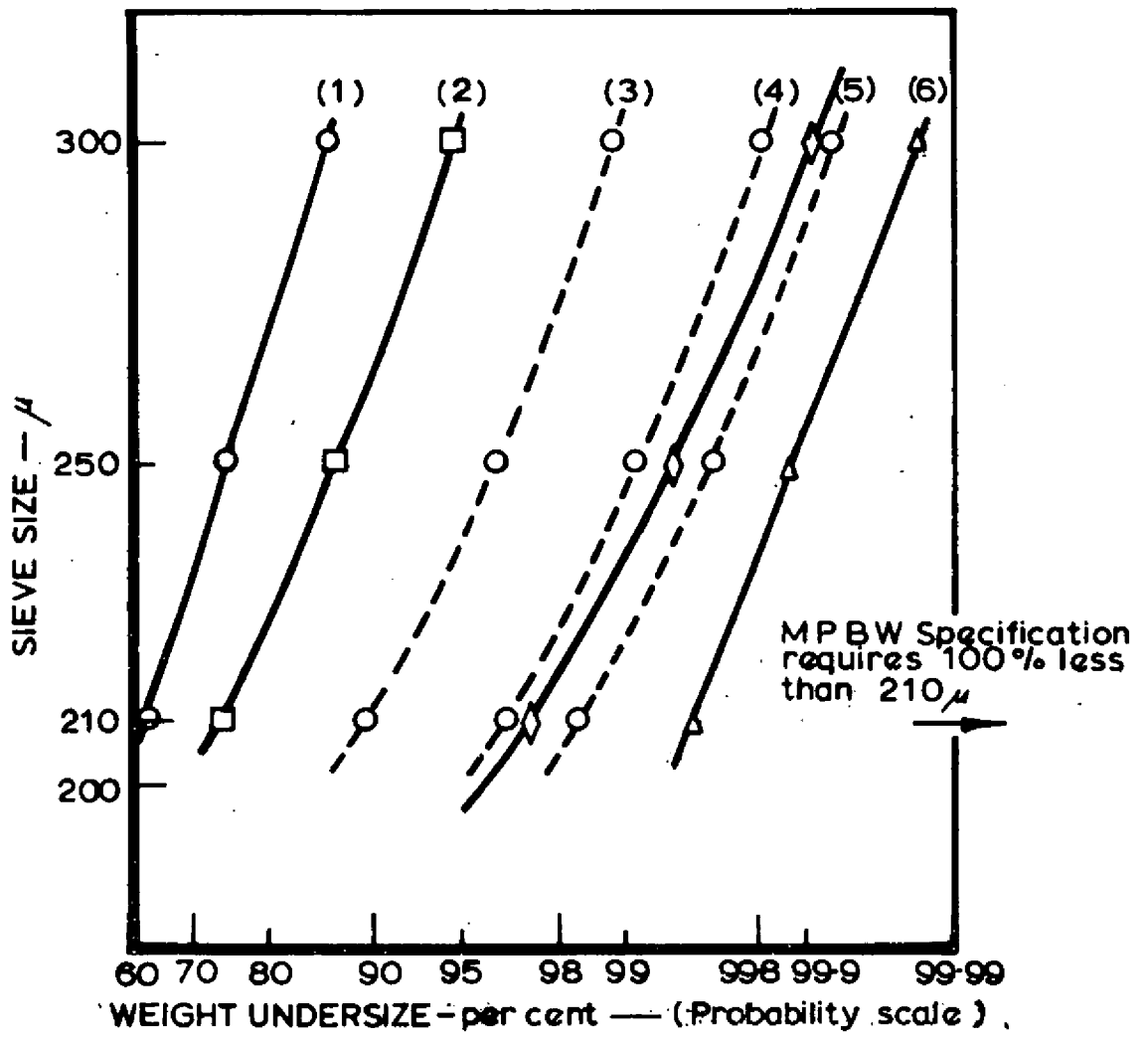


FIG.1. EFFECT OF GRINDING TIME ON PARTICAL SIZE

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- O — Powder G
- — Powders C and D
- ◇ — Powder A
- △ — Powder B

Grinding Times

- Curve(1) — 0 hours
- Curve(2) — $\frac{1}{2}$ hour
- Curve(3) — $1\frac{1}{2}$ hours
- Curve(4) — $2\frac{1}{2}$ hours
- Curve(5) — 3 hours
- Curve(6) — 4 hours

FIG.2. RESULTS OF SIEVE ANALYSIS

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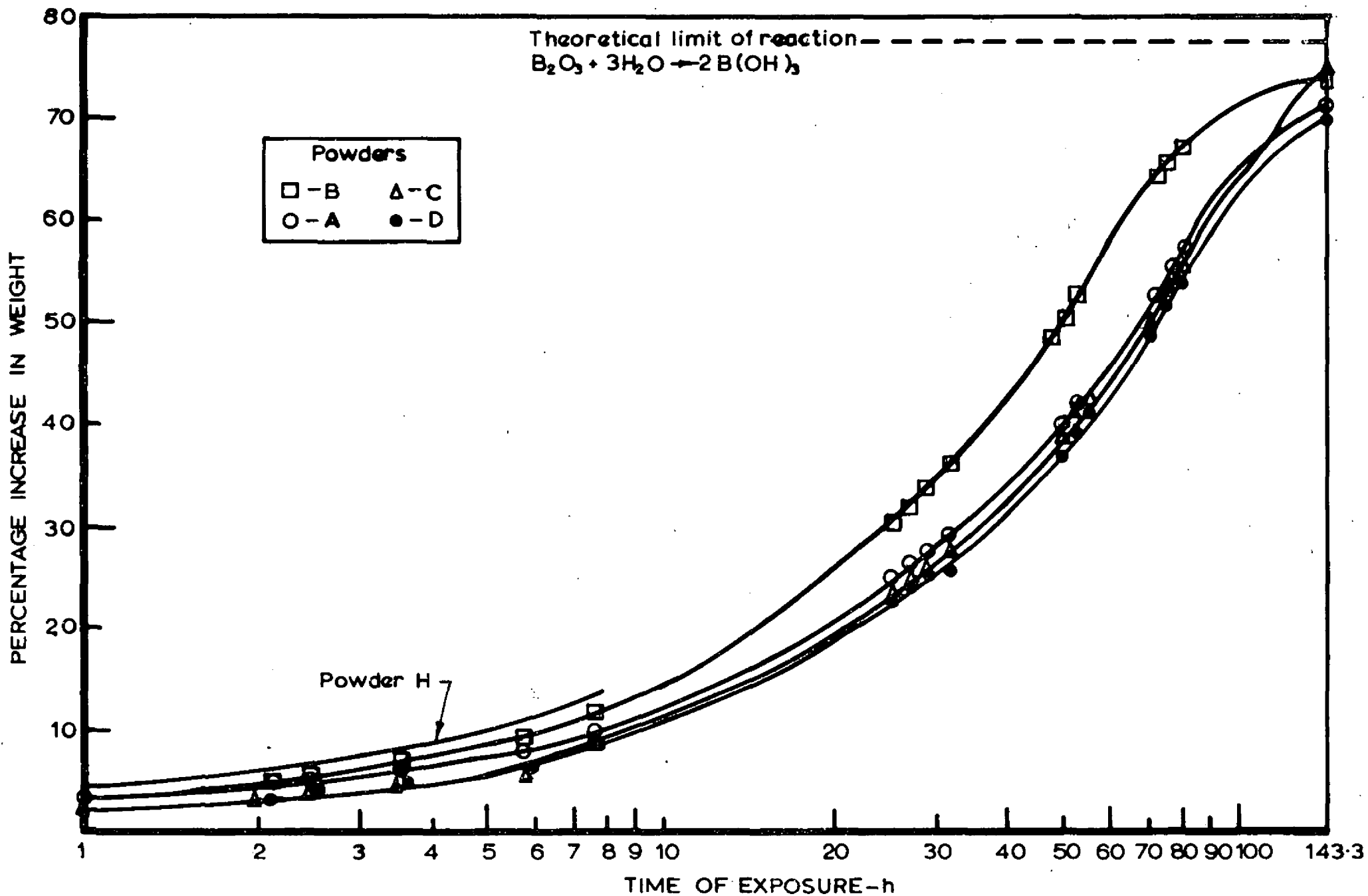


FIG.3. MOISTURE ABSORPTION CURVES FOR FINE BORIC OXIDE

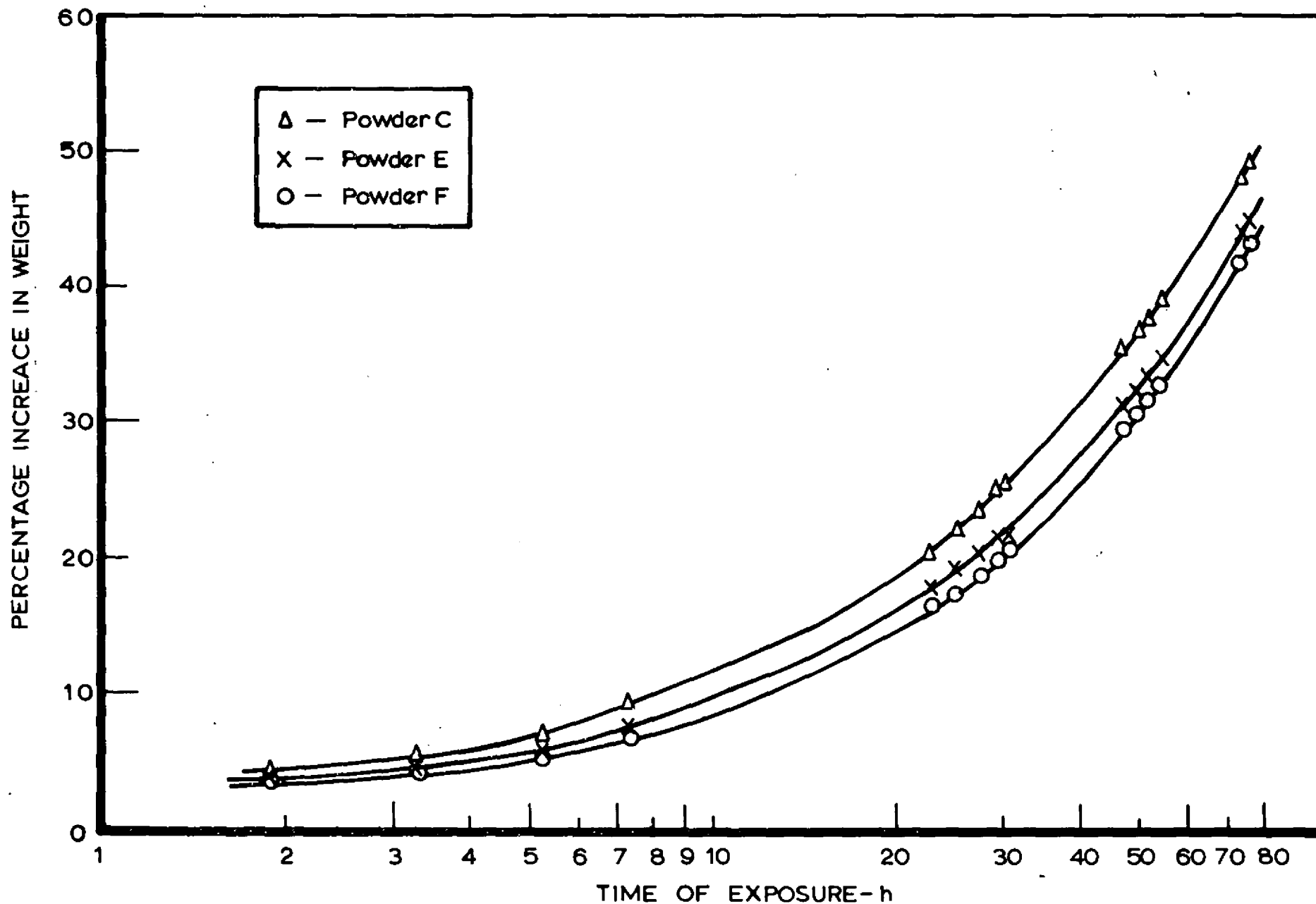


FIG.4. MOISTURE ABSORPTION CURVES FOR COARSE BORIC OXIDE

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