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A.R.D. EXPLOSIVES REPORT
Nº 612/46.

THE DEVELOPMENT OF AN ELECTROSTATICALLY SAFE LEAD STYPHNATE COMPOSITION AND THE REPRODUCTION OF LEAD STYPHNATE MIXTURES BY WET PROCESSES.

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ARMAMENT RESEARCH DEPARTMENT

Woolwich, S.E.18.

Explosives and Intermediates Branch

October 1946 A.R.D. Explosives Report No.612/46

The Development of an Electrostatically Safe Lead Styphnate Composition and the Reproduction of Lead Styphnate Mixtures by Wet Processes

This report contains no information of overseas origin.

Ref.X.30/24/7

Introduction:-

A major and notorious objection in the use of lead styphnate for Service requirements has been the combination of its readiness to acquire electrostatic charges with the very low spark energy required for ignition which is generally recognised as constituting considerable hazard in the preparation and handling of the material. Accidents have occurred during the processing of lead styphnate compositions which have been attributed to the build up and discharge of electrostatic charges during such operations as drying and sieving. Elaborate anti-static precautions have therefore been taken during the handling of dry lead styphnate compositions by the adoption of conducting containers and floors, earthing of operatives etc. but the risk of accidental ignition cannot be eliminated whilst the composition itself remains highly electrically insulating and susceptible to low energy spark discharges.

The incorporation of an inert conducting material appeared to offer a means of modifying the lead styphnate by increasing the conductivity so that an electrostatic build up would be prevented. Thus if the composition acquired a sufficient electrical leakage value, the ignition energy level of the lead styphnate would not be reached and the hazard from electrostatic ignition during processing and handling generally would be considerably reduced.

In 1944 there was a Service requirement for an electrically ignited cap composition for use in the 20 mm. Hispano ammunition. This urgent requirement was met by the production of a small particle size lead styphnate (A.R.D. Explosives Report 281/45) which was mixed in the dry state with powdered graphite to form a non-segregating mixture. It was considered that the investigation of an electrostatically safe lead styphnate composition could conveniently be extended to include the possibility of developing a wet method for the incorporation of powdered graphite. The object would be directly to produce a composition suitable for the 20 mm. electric cap thus obviating the need for dry mixing of lead styphnate.

During investigations on the incorporation of graphite in its various forms, it became apparent that a wider principle could be embraced. The dry-mixing of sensitive explosives in the factories is not a desirable process although it is a common practice. There is primarily the increased hazard of accidental explosion due to mechanical agitation and the greater number of handling operations. Then the difficulties inherent in preparing homogeneous mechanical mixtures of two or more components differing in particle size, shape and density are followed by the possibilities of segregation during subsequent handling and storage. Thus from every aspect the employment of wet processes to give non-segregating mixtures affords considerable advantages especially when the explosive concerned is lead styphnate.

The name lead styphnate is commonly applied to the chemical substance normal lead trinitroresorcinate monohydrate ($C_6H(NO_2)_3O_2.Pb.H_2O$) but for use as an explosive and particularly in connection with investigations as described in this report it is necessary to specify further its physical form in terms of such factors as crystal habit, size, surface area, degree of aggregation etc. This has been adopted for particular types designated R.D.1302 and R.D.1303 (A.R.D.Explosives Report 286/45, 281/45).

Objects of the Report

1. To give an account of the development of a lead styphnate composition, incorporating 2 - 3 per cent. graphite, which is insensitive to electrostatic discharges.

2. To detail the development of a process for the production of a composition suitable for the 20 mm. Hispano Electric cap.

3. To show the possibilities of obtaining non-segregating mixtures by wet processes.

Summary

A method has been developed by which colloidal graphite can be incorporated with lead styphnate, directly after manufacture without isolating the explosive in the dry state to give products which, in the loose dry condition will not ignite or detonate when subjected to electric sparks of high energies.

Such compositions have been prepared by the use of water dispersed colloidal graphite together with the use of gelatin solution as an agent for the irreversible attachment of graphite flocculi. This application of gelatin has been followed by extending the investigation to include related substances showing that alkaline solutions of amino acids may be similarly employed.

The process is particularly adaptable to R.D.1303, which after precipitation and washing can be treated with an aqueous dispersion of colloidal graphite equivalent to 2 per cent. of the product, followed by the addition of gelatin solution.

Untreated R.D.1303 has a high electrical specific resistance in the loose state ($> 10 \times 10^7$ ohms/cm^2). The graphited material containing 2 per cent. graphite has a comparatively low specific resistance ($< 50 \times 10^4$ ohms/cm^3), self electrification is negligible and the loose material can be subjected to spark energies of 6,200 ergs without ignition whereas the untreated R.D.1303 gives 5 per cent ignitions at spark energies of 110 ergs. The graphited R.D.1303 when mixed dry with powdered graphite fires satisfactorily in the 20 mm. electric cap test.

The process is critically dependent on sufficient colloidal graphite being incorporated with the lead styphnate to give a product of low specific resistance; for safety purposes it is considered that the material should have a specific resistance not greater than 50×10^4 ohms/cm^3 when determined by the method described.

The quantity of colloidal graphite incorporated to give the desired specific resistance depends on the type of parent lead styphnate. Lead styphnate prepared by the R.D. method (that is by the preliminary precipitation of the basic salt) with a surface area equivalent to 1,000 cm^2/g. requires a minimum of 2.5 per cent. graphite; material of surface area approximating to 700 cm^2/g. requires at least 2.0 per cent. graphite while lead styphnate of surface area 450 cm^2/g. requires a minimum of 1.7 per cent. graphite. There is some evidence that when the quantity of colloidal graphite incorporated is less than the minimum value, the product becomes more sensitive to static charges than the untreated lead styphnate. This may provide an explanation of the reported abandonment in Germany of attempted graphiting of lead styphnate associated with the incidence of serious accidents.

In general, the smaller the particle size of the lead styphnate the greater the ease of graphiting. Crystal habit is not a critical factor with lead styphnate of specific surface area greater than 600 cm^2/g. but it is difficult to incorporate sufficient colloidal graphite to obtain a product of low specific resistance below this figure, the crystal habit becoming important, and the success of the graphiting process depending on previous surface treatment of the lead styphnate.

The experimental procedure of a "non-static" lead styphnate on the 6 oz. scal is detailed in Appendix I, the process having been developed with a view to its extension to the factory scale utilizing available equipment.

In view of the satisfactory manner in which colloidal graphite could be attached to the crystals of R.D.1303, it was reasonable to expect that an increase in the graphite content of the non-static type of material would produce a composition suitable for use in the 20 mm. electric cap without the necessity for the addition of powdered graphite. Up to 7.8 per cent of colloidal graphite has been incorporated but attempts to increase the incorporation beyond this amount have caused segregation of the graphite flocculi in the wet state. R.D. 1303 takes up about 3 per cent. of the colloidal graphite as a partial coating, graphite in excess of this, up to 7.8 per cent. forming conglomerates of graphite containing crystals of R.D.1303. In the 20 mm. cap test, R.D.1303 incorporated with 7.4 per cent colloidal graphite fires within the specified voltage range but the firing resistance is extremely high.

By the use of colloidal graphite dispersed in carbon tetrachloride or acetone, up to 13.6 per cent. graphite has been incorporated satisfactorily with R.D.1303. The graphite dispersed in carbon tetrachloride affords a particularly simple process but the products are unsatisfactory in the 20 mm. electric cap.

At this stage in the investigation it became evident that the incorporation of colloidal graphite would not give a satisfactory cap composition and attention was turned to the wet incorporation of powdered graphite with R.D.1303. By replacing the aqueous colloidal graphite, as used in the graphiting process, by a suspension of powdered graphite in water and increasing the quantity of gelatin subsequently added, products have been obtained which fire satisfactorily in the 20 mm. cap test. A minimum of 0.6 per cent. gelatin is found to be necessary to effect the attachment of 10-12 per cent. powdered graphite to the R.D.1303, the addition of insufficient gelatin causing segregation and removal of the graphite during the washing processes.

An important feature of the wet mixed products containing 12 per cent. graphite is that the values of specific resistance are low indicating a low static risk whereas the dry mixed material gives a specific resistance figure associated with a high static risk. It is of interest to note that a reduction in the graphite content of the wet mixed material to 9.2 per cent. gives a product of high specific resistance.

Further investigation has established that a combination of the graphiting process using colloidal graphite and the wet mixing process will give a more easily processing type of product, with a low static risk which is independent of the amount of powdered graphite added. The process has been extended in the laboratory to the 5 oz. scale and the product, containing a total of 12.1 per cent graphite, fires within the specified limits for the 20 mm. cap test.

Four types of composition which have fired satisfactorily in the 20 mm. cap test can be listed :-

Type	Description of composition	Method of preparation	Sp.Res. ohm x 10^4/cm^3	Detonations in Megger test
I	R.D.1303 + 12.5% powdered graphite.	Dry mixing	>10,000	Detonated
II	" " " " "	Wet mixing	19	No detonation
III	R.D.1303 + 2.5% colloidal graphite + 10% powdered graphite.	Wet combination Process	2.8	No detonation
IV	Graphited R.D.1303 (2.9% colloidal graphite) + 8.8 per cent powdered graphite	Dry mixing	0.43	No detonation

Composition I is sensitive to static discharges and detonates easily in the loose state, composition II is a "non static" composition, and the material has a similar appearance to Composition I under the microscope; i.e. an intimate mixture of R.D.1303 and graphite particles. Compositions III and IV are both virtually insensitive to static charges in the loose state and under the microscope show that the crystals of R.D.1303 are partially coated with graphite particles.

Of the four compositions listed above the most satisfactory type of product from the manufacturing point of view would be Composition III. The dry mixing of graphited R.D.1303 and powdered graphite (Composition IV) would offer no difficulties, but the mixing process would be limited to 8 oz. batches with existing type of equipment.

Aluminium powder has also been incorporated by a wet method with R.D.1303 and non-segregating products containing up to 20 per cent. aluminium have been prepared. Aluminium powder with a surface area greater than 950 cm^2/g. incorporates satisfactorily with R.D.1303; powders of lower specific surface area show segregation in the wet state; while powders with surface areas about 6,200 cm^2/g. have been found to be reactive in contact with water and usually have a high oxide content. In spite of the low specific resistance of some samples of aluminium incorporated, it has not been possible to obtain a conducting composition by the use of aluminium. The method of incorporating aluminium powder might find some practical application in such mixtures as A.S.A. etc. where the aluminium powder is mixed in the dry state.

As an extension of the wet processing for mixtures with lead styphnate, aluminium stearate has been incorporated with R.D.1303 to give compositions in a variety of physical forms.

Discussion

The mechanism of the colloidal graphiting process may be considered to occur thus - the addition of a colloidal graphite dispersion to a suspension of lead styphnate in water causes the partial flocculation of the graphite by the usual effect of an electrolyte (in this instance saturated lead styphnate solution) on a hydrophobic colloid; the flocculi still retain a small residual positive charge and the flocculation rate is slow. At this stage the flocculi do not become attached to the crystals of lead styphnate, but would eventually separate out to form a separate layer. The subsequent addition of gelatin, exerts a sensitizing action and causes rapid flocculation of the graphite, at the same time the gelatin is adsorbed on the crystals of styphnate. On adsorptio the gelatin micellae become orientated so that a negatively charged group projects into the dispersing liquid. The graphite flocculi, which still carry a small residual positive charge attach themselves to the polar negative end group of the gelatin micellae, thus becoming anchored to the lead styphnate crystals by bridges of gelatin.

The amino acids behave in the same way as gelatin but only if an alkali is added; this may be accounted for by the fact that the amino acids to a limited extent resemble gelatin in regard to their sensitizing and adsorption effects. The sensitizing and protective effects of gelatin however are probably greater than those of the amino acids and it is necessary to increase the concentration of the electrolyte by the addition of ammonia or other alkali before the flocculating value of the sensitizer is reached, also in the presence of alkali the amino acids from micellae and the adsorptive power of the material is enhanced.

The electrical characteristics of the deposition or incorporation of either colloidal or powdered graphite and lead styphnate, depends on a number of factors, the main principle being the provision of a suitable number of graphite contacts to allow the free leakage of electrostatic charges. The results of the specific resistance measurements can be considered as a quantitative assessment of the following factors.

1. Lead styphnate surface area and crystal habit.
2. Graphite particle size and shape.
3. Distribution of graphite on the crystal faces or as a mixture.
4. Surface treatment effects due to adsorption of hydrophilic colloids used as protective colloids for a graphite dispersion, or gelatin used to procure adsorption.
5. Surface condition of the untreated lead styphnate,

The failure of aluminized lead styphnate to give a conducting composition may be due in part to the reactivity of aluminium with water to form a non-conducting film of oxide.

Further developments

(a) Preliminary trials have been started with the object of applying the laboratory processes on a technical scale to include the manufacture of the following types of lead styphnate compositions :-

(1) A general purpose, non-static, dust-free lead styphnate. From considerations apparent in the results already obtained this would broadly consist of the R.D.1302, R.D.1303 product treated with 2 per cent colloidal graphite by the gelatin method.

(2) R.D.1303 in non-static form as an electric cap composition ingredient.

(3) A complete non-static electric cap composition by combination process of treatment of R.D.1303 with both colloidal and powdered graphite.

(4) Non-static treatment of lead styphnate generally (including service or commercially supplied forms).

(b) It is considered that the results obtained justify a more detailed study of the mechanism and application of attachment of sols and suspensions to crystal surfaces on the general basis of crystal-suspension-bridging substance. This should include determination of electric charge on the various surfaces involved together with measurement of particle sizes starting with the substances already investigated but covering a wider range of conditions. For example although this report includes data for both colloidal and powdered graphite there is a further range available in the so-called colloidal carbon blacks, The function of the gelatin or amino acids as bridging substances or sensitisers could be further investigated possibly in conjunction with the preparation and deposition of lyophobic sols of known characteristics.

Extension of the methods to other substances has already shown promise and justifies further study. For example non-segregating mixtures of graphite/lead azide and lead dinitroresorcinate/lead azide have been prepared. It has been found however that some substances will not respond to those precipitation methods indicating that at present no simple classification could be proposed.

Appendices

I. The preparation of a lead styphnate composition with a low static risk.
II. Incorporation of high proportions of colloidal graphite with lead styphnate (R.D.1303).
III. Graphiting of R.D.1302 and other varieties of lead styphnate.
IV. Graphite wet mixing processes.
V. The wet incorporation of aluminium powder and aluminium stearate with R.D.1303.
VI. Method for the determination of the specific resistance of initiatory materials.

Illustrations

Fig.1. CG3. Graphited R.D.1303, 1% gelatin and 3.7 per cent. colloidal graphite.
Fig.2. CG19. 120 grm. batch graphited R.D.1303, 1.8 per cent. colloidal graphite and 0.2 per cent gelatin.
Fig.3 CG19. Enlarged crystal of Graphited R.D.1303 showing partial coating of R.D.1303.
Fig.4 Graphited R.D.1303 mixed with powdered graphite.
Fig.5. Untreated R.D.1303 (S.23)
Fig.6 Untreated R.D.1303 mixed with powdered graphite.
Fig.7. Relation between graphite content and specific resistance for three types of lead styphnate.
Fig.8. Flocculated graphite and R.D.1303 before the addition of gelatin.
Fig.9 CG9 graphited R.D.1303 containing 6.24 per cent. colloidal graphite (2% gelatin).
Fig.10 CG8 graphited R.D.1303 containing 4.5 per cent. colloidal graphite (1% gelatin).
Fig.11 CG11 graphited of R.D. 1303 using colloidal graphite dispersed in acetone (7.36 per cent. graphite).
Fig.12 CG13. Graphited R.D.1303 using colloidal graphite dispersed in CCl_4 (7.65% C).

Fig.13 CG15. Graphited R.D.1303 using colloidal graphite dispersed in CCl_4 (12.6% C).
Fig.14 CG36. Graphited R.D.1302
Fig.15 CG61. Graphited Service Styphnate
Fig.16 A, B & C. Particle size distribution graphs.
Fig.17 CG97. Tabular type lead styphnate of low specific surface area
Fig.18 CG102. Equant type lead styphnate
Fig.19 CG34. Wet incorporation of 12.5 per cent powdered graphite (0.6% gelatin)
Fig.20 CG60. Combination process (130 gm. scale)
Fig.21 AS.2. 10% incorporation of fine aluminium powder
Fig.22 AS.3. Incorporation of coarse aluminium powder
Fig.23 AS.4. Incorporation of intermediate size aluminium powder
Fig.24 D.S.12 Incorporation of 10% aluminium stearate
Fig.25 D.S.8 Incorporation of 10% aluminium stearate using a solution of stearic acid in alcohol.
Fig.26 Apparatus used for specific resistance tests.

APPENDIX I

Preparation of a Lead Styphnate Composition with a low Electrostatic risk

The investigation detailed below was undertaken in conjunction with the development of a dustless, small particle size lead styphnate which was eventually developed as R.D.1303 (R.D.Explosives Report 281/45). During the early work on graphiting, experimental batches of lead styphnate were used, but trial methods have been worked out using the standard type of R.D.1303, prepared on the manufacturing scale.

Preliminary investigations showed that on adding a suspension of colloidal graphite to a suspension of R.D.1303, the colloidal graphite was flocculated with subsequent segregation; the graphite could be removed almost completely by washing. From preliminary qualitative experiments it was found that if gelatin was added to the mixture, the flocculated graphite became attached to the lead styphnate and could not be removed by vigorous water washings.

Experimental

A selection of the experimental work is tabulated in Table I where the general procedure is detailed; a final laboratory method being given later in this Appendix.

The lead styphnate in C.G.2. and 3 was weighed out dry, but it was found that the wetting of the material without the use of a wetting agent was difficult, in subsequent batches therefore the lead styphnate was used in the wet condition as obtained from preparations before the drying operations. When using a new batch of lead styphnate it was found convenient to dry a known volume of the wet styphnate, weigh, and so determine the ratio of wet volume to dry weight. By this procedure, the hazard of handling dry lead styphnate was avoided and facilitated the safe production in the laboratory of up to 6 oz. of graphited lead styphnate.

Considerable variations in dilution and turbulence were shown to have little effect on the final product. The ratio of water to lead styphnate was varied from 1.25 :1 to 5.5:1. The latter water: lead styphnate ratio was used in order to make the procedure adopted in Expt.C.G.19/2 comparable with the dilution required for a proposed factory scale graphiting.

In C.G.2, after the addition of approximately 2% graphite (calc. on the lead styphnate) there appeared to be an equal distribution of graphite between the mother liquor and the lead styphnate, the graphite appeared to have flocculated to some extent and on allowing to settle, a ring of graphite was seen as a top layer. When the mixture was stirred and the gelatin solution added, the mixture settled rapidly, giving a clear mother liquor. Subsequent water washing of the product showed that no graphite was removed; there was some difficulty however in processing, probably due to the state of aggregation caused by the use of a large excess of gelatin.

The addition of 6% colloidal graphite followed by 1% gelatin solution as in C.G.3. showed that a large portion of the graphite was not attached to the lead styphnate, which, after processing with vigorous water washes, contained 3.76% graphite. The specific resistance of the final material showed a great reduction compared with that of the original styphnate.

There was some difficulty in processing the early batches of graphited R.D.1303, apparently due to the aggregation of the product; a reduction in the quantity of gelatin used overcame the processing difficulty. The incorporation of 1.9% graphite was readily achieved by the use of only 0.2% gelatin, calculated on the lead styphnate (C.G.16) and the remarkably good processing and low specific resistance of the product showed that the gelatin added should be as low as possible.

In C.G.17 the gelatin solution was added to the lead styphnate suspension before the addition of the colloidal graphite; this procedure appeared to retard the flocculation of the graphite, resulting in a mother liquor which contained a large proportion of graphite and on washing the product all the graphite could be removed.

For the incorporation of 3% graphite by the procedure of C.G.16 it was found that the subsequent addition of 0.2% gelatin was insufficient for the complete incorporation of the graphite; it was necessary to increase the gelatin to 0.3% to give a non-segregating product (C.G.18).

A reduction in the graphite content of the graphited lead styphnate to 1.6 per cent. (C.G.20) gave a product which processed well but had an extremely high specific resistance.

From the experimental work it appeared that 3% graphite could be incorporated on the R.D.1303 (i.e. specific surface area 712 cm^2/g) to give a material in which all the graphite was used as a partial coating on the R.D.1303 crystals, if however, the quantity of graphite added was increased much beyond the 3%, the excess graphite became aggregated into large masses in which some crystals of lead styphnate were included. The aggregating effect can be seen in Fig.I.

A review of the 10 and 20 grm. batches has shown that the procedure adopted in C.G.16 would serve as a basis for increased scale experiments; C.G.19 prepared on the 5 oz. scale reproduced the product of C.G.16 and provided suitable material for electrification tests, firing tests etc.

The test described later indicated that the product from C.G.19 had a low electrostatic risk in the loose state.

In view however of the relation between the graphite content and the specific resistance (see fig.7) it was considered that the graphite content of C.G.19 was too near the minimum graphite value, as a rapid increase of specific resistance of the graphited R.D.1303 was shown as the graphite value decreased from 18 per cent. to 1.6 per cent. A tentative low limit on the graphited R.D.1303 was therefore proposed as 2 per cent.

Batch C.G.19/2 was prepared in the laboratory on the 6 oz. scale at a dilution comparable with that which would be used for the graphiting of a 15 lb. batch of R.D.1303 using available plant.

6 oz. Scale

Experimental Details for the Graphiting of R.D.1303, Incorporating 2.5% Graphite

Quantities		Conditions	
R.D.1303 Lot S.23 (160 g. dry wt.)	112 mls.	Temp.	20-22°C.
water	890 "	Time of gelatin addition	3 mins.
Diluted Aquadag 3.6 per cent. C(W/V)	112 "	Stirring (extra)	5 "
Gelatin 1 per cent. soltn.	50 "	Settling time	5 "

Apparatus

31 squat beaker; 4" S.S. paddle; stirring speed 200 r.p.m. (no baffle used).

Procedure

The volume of wet lead styphnate was transferred to the beaker and stirred with the required volume of water, the diluted Aquadag was added followed by the gelatin solution. After allowing to stir for a further 5 mins. the mixture was allowed to settle and the clear mother liquor decanted. The product was washed twice with water, once with alcohol, and dried by drawing a current of air through it in a manner similar to that used for the drying of Service Azide. After drying the product was finally sieved through 100 mesh sieve.

Product

The final product consisted of a dark brown, free flowing material. Microscopic examination showed practically no increase in the state of aggregation compared with the initial material S.23 (c.f. figs. 2 and 5). The individual crystals were partially coated with graphite and portions of the free crystal surfaces could be seen (fig.3).

Graphite content	2.56 per cent.
Specific Resistance	2.5×10^4/ohms/cm^3

Notes on the process

On addition of the Aquadag to the lead styphnate suspension the mixture became almost black; after addition of the gelatin solution, the mixture assumed a deep brown colour as the graphite became attached to the lead styphnate crystals. Fig.8 shows the flocculated graphite before the addition of gelatin solution.

Generally the quantity of graphite incorporated depended on the crystal size and the amount of gelatin added. An insufficiency of gelatin was indicated by a dark coloured and slow settling mother liquor, while an excess of gelatin would cause caking on drying which causes difficulty during sieving operations. Segregation was easily noticed if the mixture was given a swirling motion when any tendency to segregation would be affirmed by a black ring of graphite appearing as an upper layer.

Electrification Properties

Complete electrification tests were carried out by S.E.R. (Swansea) on the batch C.G.19 (1.8% graphite) which represented a graphited lead styphnate with a graphite content near the minimum value, comparable with a low specific resistance. Preliminary tests on the batch C.G.19/2 (2.56%) showed the material to be even less prone to electrostatic risk than that for C.G.19 reported below (Ref.X.30/2/2).

Pouring Test

15 grms material poured from an earthed tray to an insulated aluminium catchpot from a height of 7" (R.H. 40 per cent).

Service lead styphnate	-3 e.s.u./g.
Graphited R.D.1303 (C.G.19)	+ 0.03 e.s.u./g.

Sieving Test

Material sieved through an earthed 85 mesh sieve and collected in an insulated catchpot (R.H. 40 per cent.)

Service Lead Styphnate charge devel.	-20 e.s.u./g.
Graphited R.D.1303 C.G.19 "	-6 "

These results on pouring and sieving therefore showed that this type of product had low self-electrification properties.

Spark Ignition of loose material

Loose heaps of the material were subjected to electric spark discharges of known energy.

Service Lead Styphnate:-	5%	ignitions	spark	energy	110 ergs.
	50%	"	"	"	390 "
Graphited R.D.1303 (C.G.19)	0	"	"	"	6,200 "

With higher voltages (> 1,500V) the material was blown away. 35% partial ignitions with spark energy of 55,000 ergs.

Spark ignition of pressed pellets

When pressed at 20,000 lb./sq.inch 30% ignitions occurred at spark energies as low as 17 ergs. No direct comparisons are available with Service Lead Styphnate, but the mechanically mixed 20 mm. cap composition under similar conditions of test gave 10% ignitions at a spark energy of 7 ergs.

Use in 20 mm. Electric Cap

Batches of C.G.19 and C.G.19/2 have been found satisfactory for use in the 20 mm. electric cap composition when mixed with powdered graphite to give a total graphite content of approximately 12 per cent.

Mechanical Dry Mixing of Graphited R.D.1303 with powdered Graphite

An 80 gram mix was made using dry C.G.19/2 and powdered graphite (Achesons 35), the final graphite content being 10.77 per cent (calculated graphite 10.8 per cent). The product fig.4 flowed extremely well with no adhesion to the sides of the jelly mould mixer. No segregation of graphite was observed in the product even after such drastic treatment as tapping the sides of a long vertical cylinder containing the material.

Specific Resistance

The specific resistance of the loose material is extremely low (0.43 x 10^4 ohms/cm^3), indicating a material capable of allowing the very rapid leakage of electric charges.

R.D.1303 mixed in the same way with 12% powdered graphite gave a material with a high specific resistance (>10,000 x 10^4 ohms/cm^3) i.e. similar to the untreated R.D.1303.

Ignition

Preliminary tests showed that it was difficult to ignite the C.G.19/2 mix by electric discharge and other electrification properties were similar to those of C.G.19 (Q.V.) i.e. no ignitions up to 6,000 ergs.

The pressed pellet of C.G.19/2 and graphite mix as used in the 20 mm. electric cap test gave a satisfactory firing voltage of 10.5 volts and a firing resistance of 5.5 ohms.

Gelatin Substitutes for use in Graphiting R.D.1303

Although gelatin has been investigated in some detail for the graphiting of R.D.1303; the suitability of other materials to replace gelatin has also been studied.

The following substances were tried as possible replacements of gelatin:-

(1) Methyl cellulose (2) Sodium carboxy-methyl cellulose (3) Albumin (4) Casein (5) Gum arabic (6) Representatives of the classes of amino acids which have been obtained from the hydrolysate of gelatin (7) amino benzoic acids (8) amino phenols.

The substances (1) to (5) above were added as 1 per cent. solution, as in the normal procedure using gelatin. In each case up to 1% of the colloid was used and in each case the graphite segregated almost completely so that on washing all the graphite could be removed from the products.

Gelatin has a complicated structure of peptide linked amino acids and a large number of amino acids have been isolated by the hydrolysis of gelatin; the selection detailed below has been extended to a broad class of amino acids and included such possible dipolar molecules as the amino benzoic acids and the amino phenols.

(a) Aliphatic amino acids containing one amino group and one carboxylic group (dl alanine, glycine).

(b) Aliphatic amino acids containing one amino group and two carboxylic groups (Glutamic acid).

(c) Heterocyclic compounds where the nitrogen forms part of the ring and the carboxylic acid group is in the α position (1-proline).

(d) Amino acids containing a benzene ring and the carboxylic acid group in the $\overline{o}$, $\overline{p}$ or $\overline{m}$ position.

(e) Amino phenols eg $\overline{O}$, $\overline{m}$ and $\overline{p}$ amino phenols.

The general experimental work and results are detailed in Table II.

The addition of ammonia became a modification of the original procedure as it was found that the amino acids alone would not cause the desired attachment of graphite to the lead styphnate crystals and it was therefore necessary to add ammonia beyond a certain minimum quantity. The quantity of ammonia necessary was more than that required to neutralise the acid groups in the amino acid.

It will be noticed from Table II that the isoelectric points of the amino acids vary considerably while the pH of the final mother liquors of the satisfactory batches has very little variation i.e. pH 5.5 - 5.8. The strong buffering action of the liquor will be more evident when it is considered that the quantity of ammonia, as used in the experiments, when added to the amino acid solution gave a pH of 10.06 - 10.34 for the various acids used. In addition diluted aquadag (3.35% graphite) had a pH of 9.71, which value showed little change on dilution with water.

As a variation of the process the desired quantity of ammonia was added directly to the amino acid solution (as in C.G.88 and 108), but as the addition of an excess of ammonia is undesirable due to its action on the lead styphnate, it was found preferable to add the ammonia finally so that the quantity could be controlled by inspection.

In each of the experiments using the "protein" amino acids the final products gave satisfactory processing and low values for the specific resistances (Table II).

The solubilities of the amino benzoic acids in water is small, and in order to obtain solutions up to 1% it was necessary to add ammonia. In C.G.88 the solution of anthranilic acid was effected by adding the theoretical quantity of ammonia to form the ammonium salt, giving a solution of pH 8.00; after adding up to 10 mls. of the ammonium anthranilate solution, the flocculated graphite continued to segregate, subsequent addition of ammonia however caused the graphite to become attached to the styphnate crystals to give a product of low specific resistance. Solution of the amino benzoic acids was also effected in 50 per cent. alcohol to give satisfactory products when ammonia was added subsequently (C.G.89 and C.G.90).

The use of the $\overline{O}$, $\overline{m}$ and $\overline{p}$ amino phenols were shown to be unsatisfactory as a replacement for gelatin or the amino acids in the process. In each case the graphite segregated and could be washed out of the products (C.G.116, 110, 112).

Discussion

The fact that the addition of colloidal graphite to the lead styphnate suspension cuases flocculation of the graphite particles indicates a rearrangement of the electrical charges on the colloid particles. This flocculation appears to be the usual electrolyte effect with hydrophobic colloids, as colloidal graphite is flocculated by the saturated liquors from lead styphnate in the absence of solid lead styphnate. Colloidal graphite is unusual in that the particles can acquire a positive or negative charge depending on the pH of the suspension, usually the particle is positive in alkaline, and negative in acid media. The colloidal graphite used in the above experiments is stabilised with ammonia and the diluted suspension has a pH of 9.7 indicating that the graphite is positively charged. A hydrophobic colloid such as graphite begins to flocculate when the charge on the particle falls below a certain value so that theflocculi will still retain a residual charge.

In aqueous medium the graphite flocculi settle slowly and do not attach themselves to the lead styphnate crystals unless a solution of gelatin or amino acid salt is added, then the flocculi become irreversibly attached. Gelatin is recognized as one of the common protective colloids and it can be assumed that it is this "protective" property of gelatin and the amino acids which is utilized in this process. It is reasonable to assume that the property in common to the materials which effect the attachment of the graphite flocculi is that they are capable of giving dipolar ions in solution. In solution the aliphatic amino acids exist almost entirely in the dipolar form while the amino benzoic acid acts as a 50% mixture of the unchanged and dipolar forms, the position of equilibrium depending on the presence of acid or basic groups. The amino phenols however show no evidence of behaving as dipolar ions and it is significant that they will not effect the attachment of the flocculated graphite in aqueous medium.

The attachment of graphite could be explained by assuming that, on adding a solution of gleatin to the mixture of flocculated graphite and lead styphnate (R.D.1303) suspended in water, the gelatin is adsorbed on the lead styphnate crystals, the gelatin molecule is orientated so that the chain is normal to the surface of the crystal and the end group of the chain has a negatively charged group. It is possible that the partially positively charged graphite flocculi can now become attached to the polar (negative) end group of the protective colloid or amino acid salt, thus becoming anchored to the lead styphnate crystal by a bridge of gelatin or amino acid salt.

It is of interest to note that the mechanism appears to be fairly general in as much as it has been possible to graphite other initiators such as Service L.D.N.R. and Lead Azide.

Although many experimental facts appear to bear out this conception of the graphiting process, there is no adequate explanation as to why some proteins such as casein and albumen are unsatisfactory for use in the graphiting process; they have similar isoelectric points, the adsorption takes place in a self buffered medium (pH 5.5 - 6.0) very near the isoelectric point of these ampholytes. For most simple amino acids the calculation of the isoelectric points show that there is in fact a broad zone of pH values at which the ampholyte is practically isoelectric, thus glycine at pH values between 4.3 and 7.7 has a concentration of positively or negatively charged ions, less than 1% of the uncharged dipolar molecule. The function of the ammonia addition is somewhat obscure since the final pH of the mother liquor is usually 5.5 - 5.7 but an explanation is given in Appendix II where other experimental evidence is offered.

In the course of these experiments many points of theoretical interest have arisen which have not been investigated practically as they are beyond the scope of this present work.

Appendix I.

Table I.

General Materials.

Lead Styphnate:- BS52 used dry. BS.50 and S23 used wet. BS 50 and 52 are laboratory batches; S.23 is a plant scale batch (12 lb.)

Colloidal graphite:- Diluted Acheson's Aquadag. Graphite estimated.

Gelatin:- Sherman's pure kibbled made up to 1% solution.

General Procedure.

The lead styphnate is measured by volume while in the wet state, and water added. (Various dilutions were used); the mixture was stirred at room temp. 18-22°C. and the diluted aquadag added; 1% gelatin solution was then added slowly (except CG2, and 3 see Experimental). After stirring a further 5 mins., the mixture was allowed to settle, the mother liquor decanted and the product washed twice with water then once with alcohol by decantation. The graphited styphnate was dried at 30-40°C. (except CG19 and CG19/2) and sieved through 100 mesh.

Expt. No.	Experimental	Lead Styphnate		Dilute Aquadag		1% Gelatin Soln.		Process Remarks	Product	% graphite in product (%)	Specific Resistance 10^4 ohms per cm^3	Remarks
		Equiv. Dry Wt. (g)	Surface Area cm^2/g.	Strength gm/100 ml.	Graphite /100 gm. L.S. (gm.)	Vol. (mls.)	Wt. gelatin per 100 g. L.S. (gm.)					
CG 2	To Lead styphnate suspension added colloidal graphite then gelatin soln.	(BS 52) 10	-	.6	3.6	20	2	Gelatin & graphite added progressively. Segregation with 1% gelatin & 3% graphite. Difficult processing.	Dull black free flowing	-	-	Product discarded excess of gelatin.
CG 3	Addition of gelatin solution to suspension of L.S. and colloidal graphite	"		"	.6	10	1	Good settling clear ML some caking on hot drying. Some graphite removed on washing. Poor processing.	Aggregates of Black granules	3.76	3.9	This has given a low resistance type product, but product is poor see fig. 1.
CG 16	Incorporation of 2% graphite by addition of 0.2% gelatin soln.	(BS 50) 20		1.7	2	4	0.2	Rapid settling of ML clear washes. Good processing.	Free flowing dark brown. Some aggregation.	1.9	37	Satisfactory processing fires in 20 mm. electric cap when mixed with powdered graphite.

Table 1 (Continued.)

Expt. No.	Experimental	Lead Styphnate		Dilute Aquadag		1% Gelatin Soln.		Process Remarks	Product	% graphite in product (%)	Specific Resistance 10^4 ohms per cm^3	Remarks.
		Equiv. Dry Wt. (g)	Surface Area cm^2/g.	Strength gm/100 ml.	Graphite /100 gm. L.S. (gm.)	Vol. (mls.)	Wt. gelatin per 100 g. L.S. (gm.)					
CG 17	Addition of gelatin to L.S. before addition of colloidal graphite.	(BS 50) 20		1.7	2	4	0.2	M.L. very dark and obvious segregation of graphite.	Batch destroyed.			It is better to add the gelatin finally.
OG 18	Incorporation of 3% graphite by method of CG 16	"		"	3	4) +)6 2)	0.3	After 4 mls. of gelatin settling poor, further 2 mls. addition good settling and satisfactory processing.	Free flowing dull brown. Practically no aggregation.	2.87	2.1	Sp.Res. determination constant. Tested in 20 mm. cap satisfactory after adding powdered graphite.
CG 19	Increased scale of Batch CG 16	S23 (120)	712	4.1	2	24	0.2	Good settling etc. Dried in lead azide drying pot. Some caking but broke up on sieve.	Partial graphite coating. No aggregation.	1.83	43	Electrification test see Appendix I
CG 20	Increased scale of Batch CG 16 with reduced graphite	"	"	"	1.5	"	0.2	As for CG 19.	Free flowing almost black glistening product.	1.6	>1000	Note high specific resistance.
CG 19/2	160 grm. scale incorporation of 2.5% graphite (Increased dilution).	" (160)	"	3.6	2.5	50	0.3	Dilution increased to give the equivalent volume of 40 l. for a 15 lb. batch of RD. 1303. After 40 mls. gelatin added there was some segregation after 50 mls. no segregation	Similar to CG.19 but some aggregation.	2.56	2.5	Satisfactory type of material.

Table II.

Gelatin Substitutes in Graphiting R.D.1303

General Conditions

Lead Styphnate:-	S30 R.D.1303 wet.	16 mls.(≡ 20 gm.dry)
Water	made up to	10 mls.
Colloidal graphite:-	4.2% graphite	12 mls.
Gelatin substitute:-	1% solution.	4 - 8 mls.
Ammonia	1.56 N solution	As in Table

Procedure

The lead styphnate was stirred in water and the diluted aquadag added, the mixture was stirred at room temperature and the solution of amino acid etc. added slowly followed by the slow addition of ammonia. The mixture after stirring for a further 5 mins. was allowed to settle and the clear mother liquor decanted. The product was given two swirling washes to remove any unattached graphite, then finally washed with alcohol and dried in the usual manner.

CG No.	Gelatin substitute							Process Remarks	pH. of M.L.	Sp. Res. ohms. X10^4 /cm^3	% graphite	Remarks
	Name	Type	pI (lit.)	Solution	p H of Solution	Volume used (mls.)	Vol. of Am OH added finally (mls.)					
CG107	Glycine (amino acetic acid)	NH_2 CH_2 COOH	6.00	water		8	5	Slow settling but ML clear, some graphite removed on washing.	5.68	0.65	2.04	
CG 84	Glutamic acid	NH_2 CH COOH CH_2 CH_2 COOH	3.2	water	3.06	8	4	Usual flocculations; with segregation after aspartic acid addition. After ammonia addition no segregation.	5.5	0.5	2.6	
CG 85	dl.alanine α(amino propionic)	NH_2 | CH_3-CH-COOH	6.6	water	6.7	6	2	As CG 84, but there is some dispersed graphite after the addition of amino acid.	5.5	1.6	2.64	

Table II (contd.)

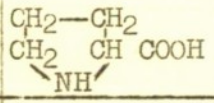
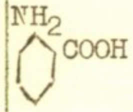
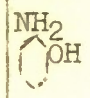
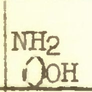
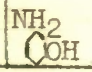
CG No.	Gelatin substitute							Process Remarks	pH. of M.L.	Sp. Res. ohms. X10^4 /cm^3	% graphite	Remarks
	Name	Type	pI (lit.)	Solution	p H of Solution	Volume used (mls.)	Vol. of Am OH added finally (mls.)					
CG 86	ℓ. proline		10.0	water	6.46	6	2	As above but settling very good.	5.54	0.62	2.26	
CG 87	Control gelatin		3-5	water	3.6	4	NIL	Good processing, rapid settling and clear liquors.	5.8	7.6	2.45	The gelatin added is slightly inadequate as there was some signs of segregation in the final wash.
CG 88	Anthranilic Acid ($\overline{O}$ amino benzoic)			Ammonia 5 mls. 1.56 N AmOH per 100 mls	8.00	10	2	Usual flocculations with segregation before the addition of the final ammonia. Good settling etc.	5.6	2.5	1.91	The quantity of ammonia added to effect solution of the amino benzoic is insufficient for attachment.
CG 89	"	"		50% alcohol	4.3	6	3	After the addition of 2 mls. ammonia there was slight segregation further ammonia addition no segregation. Good processing.	5.68	2.5	2.34	The graphiting appears to work quite well in aqueous alcohol.
CG 90	$\overline{p}$ Amino benzoic			50% alcohol		6	3	Similar to CG 89		2.2	2.2	

Table II (contd.)

CG No.	Gelatin substitute							Process Remarks	pH. of M.L.	Sp. Res. ohms. $X10^4$ /cm^3	% graphite	Remarks
	Name	Type	pI (lit.)	Solution	p H Solution	Volume used (mls.)	Vol. of Am OH added finally (mls.)					
CG108	Glutamic	NH_2 CH COOH CH_2 CH_2COOH	3.2	water + 5.4 mls. N AmOH per 100 mls.	10.2	13	NIL.	Slow settling small quantity of graphite removed by vigorous washing.	5.65	0.32	2.24	
CG116	$\overline{o}$ aminophenol			50% alcohol		6	3	Segregation after ammonia addition and complete removal of graphite on washing.	5.66	>11,000		All graphite removed in vigorous washing.
CG110	$\overline{m}$ aminophenol			"		6+4	3	As CG 109.	5.9	>11,000		As CG 109.
CG112	$\overline{p}$ aminophenol			"		6	3	As CG 109.	6.02	>11,000		As CG 109.

Appendix II

Incorporation of High Proportions of Colloidal Graphite with Lead Styphnate (R.D.1303)

Preliminary

Appendix I has shown that colloidal graphite incorporated in R.D.1303 will give a composition with a high electrical leakage value thereby reducing considerably the electrostatic risk. It was considered that an increase in graphite content of the composition, by the technique adopted in Appendix I would give a material suitable for the direct use as a 20 mm. electric cap composition. As indicated previously R.D.1303 can take up, as a partial coating, graphite approximating to 3% of its weight; graphite in excess of this becomes aggregated and is not attached to the styphnate although the masses of graphite include a certain amount of lead styphnate. Fig.6 shows the type of material which has been used for the 20 mm. electric cap and as will be seen it consists of a mixture of graphite granules (10 - 12%) and crystals of R.D.1303; on pressing the graphite granules act as a suitable "bridge" for electrical firing and it seemed probable that these conditions could be reproduced by the incorporation of graphite in excess of 3% by the graphiting process utilizing colloidal graphite.

The main advantages of such a wet process using colloidal graphite are clearly that the dry mixing of the lead styphnate would be eliminated and the final composition could offer a higher standard of uniformity in both manufacture and subsequent handling than a mechanical mixture.

Experimental

Use of Water Dispersed Colloidal Graphite

The general conditions and a selection of the experimental work is set out in Table III. The early experimental work was carried out using a laboratory batch of R.D.1303 which was weighed out in the dry state, but later, batches were measured out wet as detailed in Appendix I.

In Expt. CG4 a fairly concentrated colloidal graphite suspension was used and some difficulty was experienced in measuring the required volume, in later experiments a more dilute suspension was used. The concentration of the graphite suspension appeared to make little difference to the effective graphiting of the lead styphnate.

The incorporation of 6.24 per cent. graphite (CG4) required the equivalent of 2% gelatin before a clear mother liquor could be obtained; the processing was difficult probably due to the aggregation caused by an excess of gelatin (fig.9). The product in the wet state was black and the possible segregation of graphite was difficult to determine. A repeat of this experiment (CG7) showed segregation of graphite in the wet state; indicating that an excess of graphite was being used.

The reduction of graphite to 4.5 per cent. required 1 per cent. gelatin to give a product which did not segregate in the wet state (CG8). Although some difficulty was experienced in processing, the product was an improvement, containing a more uniform size of aggregates (see fig.10). Firing tests were carried out on this material (CG8) and from the results it was evident that insufficient graphite had been incorporated as after pressing in the cap the firing resistance and the firing voltage were of a high order, 42 ohms and 30-45 volts respectively.

Attempts were made to increase the graphit content and improve the product by slight modifications of the process. Gelatin added to the lead styphnate suspension followed by the addition of colloidal graphite was unsuccessful in causing the required flocculation of the graphite; after 4 minutes stirring there was no sign of flocculi present after 21 minutes graphite flocculi were present but there was no settling of the mother liquor and apparently little attachment of the graphite to the styphnate crystals. On heating the mixture t 75°C. precipitation of the flocculi occurred and on allowing to settle, the mother liquor cleared rapidly at 75°C. cold washes however gave dark liquors and the settling was poor. A portion of the product after washing with acetone and alcohol caked hard on drying, and sieving of the material was practically impossible. To another portion of the product, formaldehyde was added in an attempt to harden the gelatin film but this procedure was unsatisfactory.

A suspension of lead styphnate and colloidal graphite containing tannic acid required only a small quantity of gelatin (0.5 per cent.) to cause rapid precipitation of the flocculated graphite which became attached to the lead styphnate crystals, the material however was very bulky in the wet state, and on drying caked so hard that sieving was practically impossible. (See CG12).

The addition of ammonia to the lead styphnate - colloidal graphite suspension to pH 11.0, facilitated the incorporation of approx. 7.5 per cent graphite (see CG21 and CG22). The product was lighter in colour than previous batches, lighter in colour even than material containing approx. 2% graphite e.g. CG19. Microscopic examination showed the material to contain many free lead styphnate crystals which probably explains the lighter colour.

Attempts at graphiting in buffered suspensions (CG24 - 26) were proved of little practical value; it was apparent that with citrate phosphate buffer, segregation of graphite occurred at pH values from 3.2 to 8.0.

Firing tests on the products from CG21 and 22 gave low firing voltages i.e. 12.2 and 11.1 volts but the electrical firing resistance of the material was extremely high. In view of the processing difficulties encountered in the graphiting experiments using water dispersed colloidal graphite, attempts were made to use colloidal graphite dispersed in organic solvents.

Use of colloidal graphite dispersed in organic solvents

Several types of "dag" (Acheson's deflocculated graphite) dispersed in organic solvents were available. Two representative types have been used in the following investigation viz. "dag" in acetone and "dag" in carbon tetrachloride. The experimental procedure is detailed in Table IV.

The "dag" in acetone was supplied as 18 per cent. colloidal graphite made up from water dispersed colloidal graphite as used in Aquadag; in use, the commercial material was diluted to give a 4 per cent w/v suspension in acetone. After the addition of the acetone "dag" to the suspension of R.D.1303 in 50 per cent. acetone (CG10) there was some indication of flocculation although the flocculi were small and did not settle very rapidly or become attached to the lead styphnate crystals. The addition of a small quantity of gelatin solution caused a rapid clearing of the supernatent liquor and there was no segregation of graphite from the product. The product containing 4 per cent graphite incorporated in the above manner showed a high specific resistance; microscopic examination showed that the product consisted of many aggregates of R.D.1303 together with masses of graphite similar to fig.11. An increase in the quantity of acetone dag added, to give an incorporation of 7.36 per cent graphite, required the addition of 1% gelatin before the flocculi of graphite settled rapidly (CG11). Although there was no segregation of graphite from the product fibrous material was present. The product however processed satisfactorily and gave a low value for the specific resistance.

The products from Expts. CG10 and 11 were remarkable in that they were brown in colour similar to the colour of product obtained by the mechanical dry mixing of R.D.1303 and powdered graphite. In the process using acetone dag, the minimum graphite value appeal to be much higher than in the incorporations using Aquadag (of CG19 and CG10).

The firing tests on CG11 (7.36%) showed a high firing resistance and firing voltage, indicating that an increase of graphite was necessary.

The use of carbon tetrachloride "dag" has facilitated the incorporation of up to 13.6 per cent graphite with excellent processing. The commercial "dag" in carbon tetrachloride was supplied containing 10 per cent colloidal graphite and was prepared from oil dispersed graphite as used for Oildag. It was found that when the dispersed graphite was added to a suspension of the R.D.1303 in alcohol the graphite became flocculated and incorporated with the lead styphnate to give a non segregating mixture without the use of gelatin. The mother liquors were quite clear and no graphite was removed in the washing processes; after drying, the products showed no signs of caking and sieving was rapid. Figs. 12 and 13 show the type of products obtained which were light brown in bulk, much lighter in colour than products obtained during the incorporation of 2 per cent. graphite using Aquadag.

It will be seen by reference to figs. 11, 12 and 13 that the type of material obtained by incorporations using colloidal graphite dispersed in organic solvents differs considerably from those obtained in the Aquadag graphiting process. It is evident that the coating of individual crystals is poor; the greater part of the graphite being incorporated in conglomerates of graphite in which some crystals of R.D.1303 are included.

Specific Resistances and firing tests

As might be expected from Appendix I the R.D.1303 graphited with Aquadag incorporating more than 3% graphite gave products with low specific resistances, indicating low static risk (see Table III). Graphite incorporated from organic solvents appeared to be less effective in reducing the static risk with the lower proportions of graphite; however the products containing graphite in excess of 7.36 per cent had low specific resistances.

The 20 mm. cap tests on the series of products are of interest. Below is tabulated the results of a few firing tests.

Batch	Graphite Incorporation		Mean Firing Resist. (ohms)	Firing voltage (volts)	Graphite Powder added (%)	Mean Firing Resist. (ohms)	Firing voltage (volts)
	Type	% C					
CG18	Aquadag	2.87	450	45	8	5	9.1
CG21	"	7.4	200- 20,000	12.2	5	6.5	10.2
CG22	"	7.8	200- $>10^4$	11.1	5	6.4	10.2
CG11	Acetone-dag	7.36	>1,000	>60	-	-	-
CG13	Carbon-tetra-chloride dag	7.65	500	30- 45	-	-	-
CG15	"	13.6	500	30- 45			

Suitable test firing limits were considered to be that, 2½ grains pressed at 700 lb. should have a firing resistance between 6 and 12 ohms. and that the cap should always fire at 12 volts. From the above table it will be seen that CG18 with a relatively low graphite content gave a high firing resistance and voltage unless mixed with powdered graphite, when it behaved satisfactorily in the 20 mm. cap. The low firing resistance apparently can be easily modified by reducing the quantity of powdered graphite added. The results from CG21 and 22 are remarkable, showing a greatly decreased firing voltage but an extremely high and variable firing resistance, higher even than CG18 which contained only 2.87 per cent graphite. The addition of an extra 5% graphite by dry mixing with Achesons 615 graphite gave satisfactory firing characteristics for the products. A comparison of the firing characteristics of graphited lead styphnate prepared by using graphite dispensed in organic solvents, showed that incorporations up to 13.6 per cent. graphite, have higher firing resistances and voltages than products containing only 2.87 per cent. graphite incorporated by the use of Aquadag. It is of interest to note that an increase of graphite content from 7.65 to 13.6 per cent (CG13 and 15) has not altered the firing characteristics.

Discussion and conclusions

It has been confirmed experimentally that using water dispersed colloidal graphite, R.D.1303 can take up about 3% graphite as a partial coating; graphite in excess of this becomes aggregated, forming conglomerates of graphite containing crystals of R.D.1303.

It appears from the experimental data that gelatin can act both as a protective colloid and as a "sensitiser" according to the mode of addition. It has been shown in Appendix I that a saturated solution of lead styphnate will start flocculation of the water dispersed colloidal graphite, but it has required the addition of gelatin to complete the attachment of the graphite to lead styphnate. The incorporation of larger quantities of graphite proceeds in a similar manner at first until the maximum attachment is achieved. At this stage, the continued addition of gelatin sensitises the excess graphite sol. so that the charge on the micelle is reduced to such an extent that mutual attachment occurs resulting in aggregation with subsequent rapid settling of graphite aggregates.

In Expt. CG9 where the water dispersed graphite is added to a suspension of lead styphnate in gelatin solution the conditions are favourable for the protective action of gelatin to take effect. The hydrophobic colloid is entering into an excess of the protecting hydrophilic colloid, with the results that the micellae become less sensitive to the electrolyte, flocculation does not occur, nor is there attachment of graphite to the crystal faces of the lead styphnate.

The presence of ammonia in the lead styphnate/graphite suspension appears to assist the attachment of larger proportions of graphite. By the addition of ammonia as in Expts. CG21 and CG22, up to 7.8 per cent. graphite has been incorporated by the addition of only 0.4 per cent gelatin, whereas normally at least 2% gelatin is required (CG4). The effect of the ammonia addition may link with the effect of ammonia addition to the amino acids etc. detailed in Appendix I. It is known that, in many respects, the amino acids behave to some extent as the proteins in their sensitising and protecting action; the sensitising effect of gelatin however, is probably greater than that of the amino acids and it is thus necessary to increase the concentration of the styphnate ion by the addition of ammonia before the flocculating value of the sensitizer is reached.

Table III

Appendix II

General

Gelatin Solution - 1% solution made from sheet gelatin. Fresh every week.
Colloidal Graphite - Diluted Achesons' Aquadag
Temperature - 16-20°C. unless otherwise stated
Apparatus - 250 ml. tall beaker, 1" S.S. stirrer, 1" baffle, stirring 200-250 r.p.m.
Lead Styphnate - B.S.52 laboratory batch R.D.1303 used dry. S.23 is a 10 lb. plant batch used wet.

No. date	Experimental	Lead Styphnate (Dry wt)	Vol. water	Aquadag			Gelatin 1% soln.		Process Remarks	Product	Analysis % C	Sp. Res. X10^4 /cm^3	Remarks
				Strength % C	Vol. mls.	%C on Lead Styphnate	Vol. (mls.)	% on L.S.					
CG4 28/10/44	10% graphite and 2% gelatin.	BS.52 (10)	30	6	16.7	10	10 + 10	2	After 1% gelatin addn. poor settling. 2% gelatin, good settling. Poor sieving.	Aggregated free flowing black granules.	6.24	3.8	
CG6 1/11/44	Use of dilute Aquadag.	BS.52 (20)	20	1.53	133.2	10	20 10 10 10	2.5	Satisfactory settling after addn. of 2.5% gelatin. Segregation of graphite.	Some fibrous material in product. Discarded.	-	-	Unsatisfactory
CG7 1/11/44	Repeat of CG6 using more concentrated Aquadag.	"	25	6	35	10	30 10 10	2.5	Unsatisfactory similar to CG6.	Segregation of graphite in wet state.			Unsatisfactory
CG8 2/11/44	Incorporation of 5% graphite with 1% gelatin.	"	20	1.5	66.6	5	20	1.0	Clear mother liquor: caked on drying. Sieving difficult.	Some aggregates Black free-flowing.	4.5		Good graphite take up. 20 mm. cap test F.V. 30-40 V.
CG9 6/11/44	Addition of colloidal graphite to L.S. and gelatin suspension (final heating)	"	"	2	50	-	-	-	No flocculation of graphite. Flocculation on heating (75°C). Hardening with formaldehyde no	Discarded			

The firing voltage of products CG21 and 22 (12.2 and 11.1 volts respect.) are remarkably low in comparison with their firing resistances; it is probable that an increased graphite content would reduce the firing resistance appreciably but the processing difficulties lead to the search for a more convenient method for the incorporation of higher proportions of graphite.

The use of the colloidal graphite dispersed in organic solvents has facilitated the incorporation of high proportions of graphite; in particular incorporations using graphite dispersed in carbon tetrachloride have given products which process without difficulty.

The major difference in the mode of processing these two types of dispersions is that, with acetone dispersed graphite it is necessary to add gelatin solution to complete flocculation of graphite with attachment to the lead styphnate, whereas the graphite from carbon tetrachloride dispersion is flocculated satisfactorily by alcohol. Although 13.6% graphite has been incorporated by the method used in CG15, the firing characteristics are the same as the material from CG13 in which only 7.65 per cent graphite had been incorporated by a similar method.

The remarkable difference in colour of products from Aquadag incorporations and those obtained by incorporation from graphite dispersed in organic solvents is a result of the graphite distribution. Thus products from the former incorporations are almost black, even when the graphite content is low; it is apparent from fig.2 that all the graphite (1.83%) is attached to the crystals which accounts for the almost black colour of the product. Products obtained by use of graphite in organic solvents are light in colour, similar to the composition obtained by the mechanical dry mixing process. Figs. 6 and 12 show this similarity is more apparent under the microscope. In fig.12 there is no coating of graphite in the sense of that shown in figs.2 and 3; the lead styphnate crystals are attached to aggregates of graphite. The difference in graphite distribution can explain the differences in resistance, thus in CG10 the graphite content is 4 per cent (acetone dispersion) yet the specific resistance of the material is extremely high while in CG19 the graphite content is 1.83 per cent (water dispersion) and the specific resistance comparatively low. In the former product the surface area of the exposed graphite surface is much smaller than that in the latter, so that the carbon to carbon contacts which determines the electrical resistance in the loose state are more frequent in the material containing only 1.8 per cent. graphite.

Although the methods of graphite incorporation outlined in this appendix, have shown the possibility of incorporating high proportions of graphite and some interesting facts have been revealed, the material containing as much as 13.6% graphite are not satisfactory for direct use as a composition for the 20 mm. electric cap.

No. Date	Experimental	Lead Styphnate (Dry wt)	Vol water	Aquadag			Gelatin 1% soln.		Process Remarks	Product	Analysis % C	Sp. Res. X10^4 /cm^3	Remarks
				Strength % C	Vol. mls.	% C on Lead Styphnate	Vol. mls.	% on L.S.					
CG12 9/11/44	Addition of gelatin to a suspension of L.S. colloidal graphite and tannic acid (1.25%)	BS.52 (20)	20	1.7	59	5	10	0.5	Clear M.L. Good coating. Material bulky. Filtration difficult.	Not isolated.			Good incorporation but poor product.
CG21 13/12/44	Addition of gelatin to L.S. graphite susp. at pH 11.1 (Ammonia)	S.23 (20)	36 + 4 mls. 1.4N, NH_4OH	4.1	40	8	8	0.4	Clear M.L. Some caking. Sieving difficult pH ML 6.2	Dark free flowing. Some aggregates. Uncoated crystals present.	7.4	0.35	Firing voltage 12.2 but high resistance
CG22 13/12/44	Repeat of CG21 pH 11.3	"	"	"	"	"	"	"	Similar to CG21 pH ML. 6.02		7.8	0.19	F.V. 11.1 volts F.R. high.
CG23	Addn. of gelatin to hot suspension of L.S. & 8% graphite Temp. 70°C.	"	34 + 6 mls. N.AmOH	"	"	"	"	"	Clear M.L. Caked hard on drying. Sieving difficult pH ML 5.06	Hard aggregated particles. Large aggregates	-	-	
CG24 14/12/44	Addn. of gelatin to LS/graphite in pH 3.2 citrate/phosphate buffer.	"	3.2 pH buffer 40	"	"	"	8 + 8	0.8	Very poor settling. Filtration difficult pH ML. 4.08	Discarded.			
CG25 15/12/44	Addn. of gelatin to LS/graphite in pH 6.0 citrate phosphate buffer.	"	6.0 pH buffer 40	"	"	"	8	0.4	Poor settling with signs of segregation pH ML. 4.18.	Discarded.			
CG26 15/12/44	As CG25 but buffered at pH 8.0	"	8.0 pH buffer 40	"	"	"	8 + 8	0.8	Poor settling. Bulky material; difficult filtration. Discarded.				

Table IV. Use of "Dag" in Organic Solvents

Appendix II

General:-

Lead Styphnate - 20 gms. dry weight used. B.S.52 used dry B.S. 50 measured out wet and washed with alcohol.

"Dag" in Acetone - "Dag" in acetone diluted to 4% w/v with acetone.

"Dag" in CCl_4 - "Dag" in CCl_4 used 15% w/v

Apparatus - 250 ml. tall beaker, SS stirrer, 1" SS baffle

Procedure

The R.D.1303 stirred with acetone or alcohol; the colloidal graphite added slowly, then gelatin or alcohol as indicated in tables. The product after settling was washed with acetone or alcohol, dried at 40-50°C. then sieved through 100 mesh.

No. Date	Experimental	Lead Styphnate Batch No.	Medium (vol.) (mls.)	Colloidal graphite				1% Gelatin Soln.		Processing	Product	Analysis	Sp. Resist. ohms $10^4 cm^3$	Remarks
				Type	Graphite % w/v	Vol. (mls.)	% on LS.	Vol. (mls.)	% on LS					
CG10 7/10/44	Use of Dag in acetone slow addition of gelatin solution.	BS.52	50% aqueous acetone (20)	Dag in acetone	4	20	4	4	0.2	After 4 mls. gelatin addn. clear liquors obtained no segregation. Good processing.	Free flowing dark brown. Few aggregates.	4.0	14,000	Final liquor 75% acetone. Note high Sp. Res.
CG11 8/10/44	Increase of graphite content and acetone concentration.	"	75% aqueous acetone (30)	"	"	40	8	20	1.0	Clear liquor obtained only after 20 mls. gelatin Fibres present. Poor processing.	Similar to CG10 but more aggregates.	7.36	12.9	Firing Resist. 1000 ohms. do. voltage 60 volts.
CG13 9/11/44	Dag in CCl_4 to give 7.5% incorporation of graphite (No gelatin)	BS.50	Alcohol (20)	Dag in CCl_4	15	20 + (26 mls.) alcohol).	7.5	Nil	Nil	Graphite flocculated and precipitated onto the L.S. No segregation. Good processing.	Dark brown free flowing some aggregation	7.65	10.7	Firing Resist. 500 ohms. " voltage 30-45 volts.

Table IV contd.

No. Date	Experimental	Lead Styphnate Batch No.	Medium (vol.) (mls.)	Colloidal graphite				1% Gelatin Soln.		Processing	Product	Analysis % C.	Sp. Resist. ohms 10^4cm3	Remarks
				Type	Graphite	Vol. (mls)	% on LS.	Vol. (mls)	% on LS.					
CG14 9/11/44	Dag in CCl_4 to give 12.6% graphite. Precipitation by alcohol.	BS.50	Alcohol (20)	Dag in CCl_4	15	20 + (20 mls. CCl_4)	15	Nil	Nil	The Dag added in 3 min. separated into two layers, inefficient stirring. Increased stirring gave rapid flocculation. No segregation. Good processing.	Dark brown free-flowing. Many aggregates of large size.	12.6	1.5	
CG15 10/11/44	Repeat of CCl_4 with increased turbulence.	"	Alcohol 40 mls.	"	"	20	15	Nil	Nil	Dag added in 10 mins. rapid stirring. Immediate flocculation with attachment. No segregation, very good processing.	Light brown in colour. Many aggregates.	13.6	7.8	Firing resist. 500 ohms " voltage 30-45 v.

APPENDIX III

Graphiting of R.D.1302 and other types of lead styphnate

In view of the satisfactory results obtained by graphiting R.D.1303 using water dispersed colloidal graphite (Appendix I), the general application of the process to other types of lead styphnate was a logical requirement. From tests on graphited R.D.1303 it was considered probable that the incorporation of approximately 2 per cent. graphite with R.D.1302 would overcome the difficulty of processing an electro static sensitive material in such factory operations as drying, sieving and mixing.

Graphiting of an R.D.1302 blend

In 1942 thirteen 10 lb. batches (S.1-13) of dustless lead styphnate had been manufactured (since designated as R.D.1302 see R.D. explosives report 286/45), and as a bulk of standard material for the investigation, a 1½ lb. blend was made from batches S.1-12 (excluding S.11).

The storage history of these materials comprising the blend is of interest in view of the results obtained, which, in part depends on the surface treatment of the lead styphnate crystals. The batches of lead styphnate, packed in cloth bags had been stored under water in white pine and oak barrels for approximately two years; subsequently samples were removed from each batch and stored wet in gutta percha vessels for about six months.

A direct application of the process used for the graphiting of RD.1303 showed that the maximum graphite which could be incorporated was in the region of 1 per cent. This graphite content was insufficient to give a specific resistance comparable with a low electro static risk. Fig.14 shows that all the graphite is attached to the styphnate crystals, but it is evident that the graphite distribution is insufficient to give the required contact of graphite particles to ensure a satisfactory electrical leakage.

Attempts were made to increase the quantity of graphite incorporated by the addition of ammonia or acetic acid, but in each case, after a portion of graphite had become attached to the crystals, the further addition of graphite caused segregation. A control graphiting of R.D.1303 showed that the reagents used were satisfactory, and in addition a check on the diluted Aquadag showed that the state of dispersion of the colloidal graphite had not changed appreciably during four months.

It was considered probable that the surface conditions of the lead styphnate crystals was a critical factor in the graphiting process. Although the blended material used in these experiments had been stored for a number of years and there was some uncertainty regarding the effect of storage on the crystal surfaces, it was considered advisable to investigate possible methods for the incorporation of sufficient graphite to give a satisfactory antistatic material.

The addition of tannic acid solution to the suspension of the R.D.1302 blend showed some increase in graphite incorporation, but as segregation occurred when 2 per cent. colloidal graphite was added, the method was discarded. It is of interest to note that the addition of tannic acid equivalent to 0.2 per cent. on the lead styphnate (10 per cent. on the graphite) gave the usual flocculation of graphite when the colloidal graphite was added to the mixture. On increasing the tannin added to 0.6 per cent. (equivalent to 30 per cent. calculated on the graphite added), no flocculation of the colloidal graphite occurred even after 25 minutes. It appeared that by the addition of colloidal graphite to the suspension containing the equivalent of 30 per cent. tannin, the graphite particles became protected by the excess of hydrophilic colloid, so that flocculation, by means of the electrolyte, did not occur.

Various proportions of tannic acid, and the effect of irreversible adsorption was tried in order to obviate the protective action of tannin but there was no apparent increase of graphite incorporation. It was hoped that the tannin would become adsorbed on the crystals of lead styphnate and act as a precipitant for the gelatin causing attachment of the graphite flocculi; this however, did not happen to any marked extent.

A mixture of diluted Aquadag and gelatin added to the R.D. 1302 suspension caused flocculation of the graphite with complete segregation, there was no indication even of partial attachment of graphite, and subsequent addition of tannic acid showed no improvement.

Pretreatment of the R.D.1302 blend with gelatin, showed some improvement in the graphite incorporation. The lead styphnate was allowed to stand twelve hours in a 0.4 per cent. solution of gelatin, after which the unadsorbed gelatin was removed by water washes. The pretreated material was suspended in water, diluted Aquadag and subsequently gelatin solution, added in the usual manner. Addition of 2 per cent. colloidal graphite showed some segregation of graphite, which was removed by vigorous washing, while the product contained 1.2 per cent. colloidal graphite, and gave a value for specific resistance of 50×10^4 ohms/cm.^{3}. This value was very near that obtained for CG19 indicating that the blend, on graphiting after pretreatment with gelatin will give a material having a low electric static risk.

Graphiting R.D.1302 batch S12 after factory storage

To verify the results above a sample of one of the batches comprising the blend (batch S.12) was obtained and the investigation continued. The batch S.12 had been stored under similar conditions to the blended material except that it had been sampled directly from the 10 lb. batch a short time before use.

Graphite incorporated satisfactorily by the normal procedure to give products with low specific resistances (See Table V). A series of experiments tabulated in Table V, CG63 - CG65, showed the change in specific resistance with graphite content. Experiments reducing the quantity of gelatin added, showed that for each quantity of graphite added there is a certain minimum quantity of gelatin required for incorporation. Thus it will be seen from Table V that the minimum quantity of gelatin required for the incorporation of 1.7 per cent graphite is 0.25 per cent calculated on the weight of lead styphnate, this product (CG67) gave a very low value for specific resistance. An increase in gelatin leads to some increase in specific resistance of the final product together with aggregation, which in the case of a large excess of gelatin would affect the sieving procedure.

Graphiting of Service (I.C.I.) Lead Styphnate

The general method of graphiting R.D.1303 has been applied to the graphiting of Service (I.C.I.) Lead Styphnate and it has been shown to give a non-static product. The sample of lead styphnate was supplied dry, 20 grms. of the material were suspended in 50 mls water by stirring and 14 mls diluted Aquadag containing 3.6 grms colloidal graphite per 100 mls. added; the total volume being made up to 100 mls. with water. Gelatin solution (1%) was added slowly to the stirred mixture at room temperature; after the addition of 8 mls. gelatin solution there was signs of graphite segregation during a trial settling, the addition of a further 2 mls of gelatin solution gave satisfactory incorporation of the graphite. No segregation was observed on settling or swirling, the supernatant liquors settled rapidly and washing by decantation was rapid. The product after washing twice with water and once with alcohol was dried at 40-50° then sieved through a 60 mesh sieve.

The almost black final product showed practically no aggregates (see fig.15 CG.61). The final product contained 2.4 per cent graphite and gave low values in the specific resistance test (6.5 x 10^4 ohms/cm.^{3}) indicating a low static sensitiveness in the loose state.

Specific Resistance and Graphiting Efficiency

The graphiting of the R.D.1302 blend has in the main shown unusual results, since only a small portion of graphite has been incorporated by the standard procedure, whereas another sample of R.D.1302 and a sample of Service Lead Styphnate (I.C.I.) have graphited satisfactorily. By the pretreatment method the quantity of graphite incorporated in the R.D.1302 blend has been increased to 1.2 per cent, giving a product with a specific resistance comparable with that of CG.19 (QV) which has been shown to be practically "non-static". The quantity of graphite incorporated however, is small and would appear to be a maximum by the pretreatment method.

R.D.1302 batch S.12 has been graphited satisfactorily by the usual procedure, behaving as R.D.1303 in respect of its graphiting efficiency. The results of a series of graphitings have beenplotted in fig.7; it will be seen that the incorporation of less than 1.3 per cent graphite under the conditions used, would give a composition of high specific resistance and for material of this surface area i.e. 457 cm^2/g, this graphite content may be considered as the minimum graphite value. The minimum value may be reduced to some extent by a decrease in the amount of gelatin added. Thus the incorporation of 1.7 per cent graphite (CG.63) by the use of 0.35 per cent gelatin gave a product with specific resistance of 21.4 x 10^4 ohms/cm.^{3} compared with a value of 5.9 x 10^4 ohms/cm.^{3} when 0.25 per cent gelatin was used for the incorporation.

Effect of surface area and crystal habit on the graphiting process

In view of the difference in behaviour of the two samples of R.D.1302 and the differences in the minimum values for R.D.1302 batch S.12 and the general values for graphited R.D.1303, further investigation was desirable in order to determine, if possible, the cause of the differences.

A review of the physical characteristics of the materials pointed to a difference in particle size, thus the average diameters for R.D.1302 blend, R.D.1302 S.12, and R.D.1303 lot S.24 were 0.047 mm., .029 mm. and 0.028 mm. measured as Martin's diameter. The similarity in average particle size of the last two samples might account for the similar behaviour on graphiting, while the poor graphiting efficiency of the R.D.1302 blend may have been due to the presence of large crystals if less surface active than the smaller crystals.

Microscopic examination of the materials quoted above showed some difference in crystal habit. The R.D.1303 existed mainly as tabular type crystals, the batches of R.D.1302 blend and batch S.12 were of an equant habit.

It was clear that a determination of Martin's-diameter would be insufficient data to characterize the graphiting efficiency of various types of lead styphnate, since it was possible to have two materials of the same Martin's diameter yet differ considerably in depth of crystal. It was considered that a measurement of the surface area of the material would give a better, and more reliable basis for comparison of graphiting efficiency.

Below is tabulated the chief characteristics of the three materials discussed above.

Material	Martin's dia. mm.	Sp.Surface (cms^2/g)	Crystal type	Graphiting efficiency
R.D.1302 Blend	0.047	325	Equant	Poor
R.D.1302 S.12	0.029	457	Equant	Good
R.D.1303 S.24	0.028	822	Tabular	Good

The surface area of the blended material is small compared with R.D.1303 S.24. There is a great difference shown in the surface areas of the batches R.D.1302 S.12 and R.D.1303 S.24, yet their particle sizes are practically the same.

The investigation was continued by graphiting a series of newly made laboratory batches of lead styphnate of various types and surface areas. The methods used for the precipitation followed the general procedure adopted for the preparation of R.D. Lead Styphnate, i.e. the precipitation of a basic salt by the addition of lead acetate solution to a solution of magnesium styphnate at 75°C, and conversion of the basic lead styphnate to the monohydrate of the normal salt by the addition of nitric acid.

Tables VI, VII, and VIII, show the experimental procedure and results of a series of laboratory batches using materials as would be used for the preparation of R.D.1302 and R.D.1303. (See A.R.D. Explosives Reports No.286/45 and 281/45). The scale of the experiments were 35 gms and 50 gms; the products of precipitation while still wet from the washings were divided into three parts by volume, one portion being dried and weighed, another being used directly for the graphiting experiments and the third portion being retained wet for repeat work if necessary. Each experiment may be considered under two sections, (A) the precipitation of the lead styphnate, and (B) the graphiting procedure.

Precipitation using Magnesium Styphnate of p.H. 4.2

The precipitation procedures for the series CG.95A to CG.100.A (Tables VI and VIII) may be divided into two main classes.

(i) Long basic stage with various rates of nitric addition.
(ii) Short basic stage with various rates of nitric addition.

With magnesium styphnate of p.H 4.2 and a long basic stage, the basic salt first appeared in the usual small yellow opaque aggregates, which changed through hair crystals to columnar and nuclei type with the complete disappearance of the small aggregates; this change was completed in 19 minutes. The rapid addition of nitric acid (CG.95) gave rapid normal salt formation, 1 minute after the addition, normal salt could be seen attached to the columnar crystals, after 3 minutes, there were very few columnar crystals remaining. The final product was small (0.015 mm.) and had the characteristic appearance of R.D.1303 i.e. tabular type with aggregation of crystals. The particle size distribution polygon fig.16A and the value for the surface area (Table VIII) show that the material is smaller than the usual R.D.1303. Graphiting of this product was satisfactory if over 2.5 per cent graphite was incorporated.

Addition of nitric acid at a slower rate (3½ minutes) as in CG.96 showed that the nuclei present in the basic salt dissolved first, the normal salt subsequently appeared growing from the columnar crystals, the columnar crystals eventually disappeared leaving a product similar to CG.95 in surface area particle size, graphiting efficiency etc.

A slow addition of nitric acid (22 minutes) as in CG.97, followed the same evolution of crystal form but at a much slower rate, giving a final product consisting of large clear crystals with enlarged basal planes. On rolling the crystals through 90° in a vertical plane it was apparent that they were tabular in habit and contained many irregular inclusions and some parallel striations (see fig.17). The normal graphiting procedure was unsatisfactory with this material which behaved as the R.D.1302 blend, although the habit was tabular and the surface area greater than that of a typical R.D.1302 batch. 1.08 per cent graphite was incorporated by the addition of up to 0.57 per cent. gelatin but this quantity of graphite was insufficient to give a product of low electrical resistance.

Short Basic Stage with Various Rates of Nitric Acid Addition

Using the same magnesium styphnate as above, nitric acid was added to the basic lead styphnate at the stage when the material consisted mainly of the small yellow opaque aggregates, i.e. after 4 minutes basic stage.

Rapid addition of nitric acid (CG.98) gave rapid growth of normal salt with the transient formation of masses of hair-like crystals. The final product was small (0.020 mm.) with some tendency to aggregation. The individual crystals were of the equant type presenting a squarish profile; there also appeared to be many liquid inclusions in the product. Graphiting of this product was satisfactory.

In CG.99 the nitric acid was added at a slower rate (10 minutes); the normal salt grew more slowly than in CG.98, showing a slow transition from the small aggregates to the hair-like crystals of basic salt and finally to the normal salt. After six minutes of the nitric addition there appeared to be no change in the product. The final material had a specific surface area comparable with that of R.D.1303 (695 cm^2/g) but the individual crystals were of equant type and orientated at random. The particle size distribution has a greater range than CG.98 (fig.16B) and the material graphited satisfactorily.

During the slow addition of nitric acid (CG.100) the basic salt underwent the same transformation as in CG.99, and there was no apparent change in the normal salt after the addition of approximately half the quantity of nitric acid. The product was similar in type to CG.99 although as might have been expected, the crystals were much larger and had a smaller surface area than CG.99. (Graphiting of the product was in the main unsatisfactory). During a graphiting experiment 1.74 per cent graphite was incorporated and a mean figure for the specific resistance obtained, 72×10^4 $ohms/cm.^3$ but as the results were not consistent the graphiting experiment was repeated; by vigorous washing only 0.74 per cent graphite was incorporated and the specific resistance was high.

In the above series of experiments the range of particle sizes and specific surface areas were rather restricted, thus there was no material with a specific surface area below 500 cm^2/g so that no direct comparisons can be made with R.D.1302 which normally has a specific area of approximately 400 cm^2/g. To increase the range of surface areas a series of experiments showed that a decrease in the rate of lead acetate addition gave a large type of product.

Thus on adding the lead acetate to the magnesium styphnate in four minutes and allowing to stir for six minutes (CG.102), the first formed aggregates changed to a mixture of aggregates and hair-like crystals, which, on the addition of nitric acid over a period of 7½ minutes, changed via the hair-like crystals to large normal salt crystals. The individual crystals were mainly of the equant type although some tabular type could be seen (fig.18). The average particle size was 0.0388 mm. with a specific surface area of 305 cm^2/g and graphiting of this material showed that only a small amount of graphite could be incorporated, i.e. insufficient to give a suitable value for the specific resistance.

Variations of the R.D.1303 process

The main material difference in the R.D.1303 process from that of the R.D.1302, is the concentration and p.H of the magnesium styphnate solution. Although on the plant scale a limit of p.H 4.5 - 4.65 was set for R.D.1303 it had been found that a p.H 4.7 - 4.8 was required to give similar material on laboratory scale preparations.

For the series of experiments detailed in Table VII, magnesium styphnate of p.H 4.8 containing 184.8 g. styphnic acid per litre, has been used. Normally in the R.D.1303 process the basic stage is continued until all the initial aggregates of basic salt are replaced by acicular crystals and nuclei before the rapid addition of nitric acid. A basic salt stage of 10 minutes in expt. CG.121 was sufficient to clear the aggregates of basic salt; the rapid addition of nitric acid (½ minute) then gave a product of large surface area (1,014 cm^2/g) and tabular habit which graphited satisfactorily when 3 per cent colloidal graphite was added.

The rapid addition of nitric acid to the basic salt which still contained some aggregates, (CG.122) gave a product consisting of many large equant type crystals on which small crystals were adhering. This product had a small specific surface area (384 cms^2/g) and was unsatisfactory for graphiting by the normal procedure.

A slower rate of nitric addition (5½ minutes) to the basic salt containing no aggregates (CG.123) gave a small particle size product of large surface area (1,184 cms^2/g). The crystals were a mixture of tabular and equant type.

An extention of the addition time for the nitric acid to 17 minutes. (CG.124) resulted in a product of increased crystal size but the habit was mainly of the tabular type. The graphiting was doubtful since only 1.5 per cent graphite was incorporated by the standard method.

From the foregoing experiments (Tables VI and VII) it is confirmed that during the change over from the basic to normal lead styphnate, if aggregates of basic salt are present during the nitric addition, equant type crystals are formed which have a small surface area in spite of their rapid formation by the rapid addition of nitric acid (cf. 121 and 122). The addition of nitric acid to the basic salt containing no aggregates, i.e. consisting entirely of acicular or bladed crystals together with nuclei, results in the formation of a tabular type of normal lead styphnate, the size depending on the rate of nitric acid addition; the particle size increasing with a decrease in rate of nitric acid addition.

It will be seen from Table VIII, that of the various types of lead styphnate prepared, the crystal habit has had little effect upon the ease of graphiting. Thus CG.100 is of the equant type (sp. surface 537 cms^2/g) while CG.124 is of the tabular type (sp. surface 534 cms^2/g) and both materials behave in a similar manner in the graphiting process, i.e. they incorporate a small quantity of graphite giving products of variable resistance. Products with specific surface areas of the order 300-400 cms^2/g incorporate very small portions of graphite which gives products of high specific resistance and detonate in the 500 V. Megger test (see later). Products of surface area in the region of 700 cms^2/g graphite satisfactorily and behave in general as the normal R.D.1303 on graphiting; lead styphnates of surface area in the neighbourhood of 1,000 cms^2/g require a higher proportion of graphite to give materials of correspondingly low specific resistance; the minimum value could be set at 2.5 per cent graphite compared with 1.9 per cent for material with specific surface area of 700 cms^2/g. The specific surface area of CG.96 was 1,040 cms^2/g and incorporation of 2.14 per cent graphite gave a product of high and variable specific resistance. The incorporation of 2.68 per cent graphite was sufficient to give a product of quite low resistance. The relation between specific resistance and graphite content for lead styphnate of surface area approximately 1,000 cms^2/g is shown in fig.7.

The difference in particle size distribution is of interest, it shows the change in particle size with rate of nitric addition (figs. 16. A.B. & C). The difference in particle size distribution is comparatively great for CG.95 and CG.96 although their surface areas are practically the same. This difference is probably due to a shape factor or the state of aggregation which is typical of these materials. Again CG.98 and CG.99 show little difference in specific surface areas and behave similarly on graphiting, but there is a large difference in their distribution polygons. On the other hand comparing CG.99 and CG.100 (fig.16B) the distribution polygons are similar, but there is quite a difference in their specific surface areas; CG.99 (sp. surface 697 cm^2/g) graphites satisfactorily while CG.100 (sp. area 537 cm^2/g) is unsatisfactory for graphiting.

Summary and discussion

It is conluded that lead styphnate, prepared by the R.D.Process, will incorporate sufficient graphite by the process described, to give a product having an electrical resistance, capable of allowing the ready leakage of electric charges without detonating, if the specific surface area is greater than 650 cm^2/g.

By a gelatin pretreatment, lead styphnate of specific areas lower than 650 cm^2/g can be graphited to give electric leakage values comparable with a "non-static" lead styphnate. The ease of graphiting increases as the surface area approaches the region of 650 cm^2/g.

The difference in beahviour of the blended R.D.1302 and the particular batch R.D.1302 S.12, could be attributed in part to their difference in surface areas; the blended material (Sp. area 325 cm^2/g) not being affected in the same manner on storage, as the material of larger surface area, R.D.1302 S.12 (sp. area 457 cm^2/g). It is probable that the wet storage of these materials has been in the nature of a pre-treatment; the material with the larger surface area being affected to the greater extent.

A similar effect may be the cause of the satisfactory graphiting of service lead styphnate (I.C.I.). This material had a specific surface area of 473 cm^2/g and has been stored under similar conditions to R.D.1302 S.12. This storage is akin to a pre-treatment since freshly prepared R.D.1302 of similar surface area does not graphite satisfactorily unless it is given a gelatin pretreatment.

The crystal habit of the lead styphnate with surface areas greater than 650 cm^2/g. appears to make little difference to the graphiting process. The crystal habit of lead styphnate, with surface areas 300 to 400 cm^2/g, may have some effect on the incorporation of graphite. It might be possible to decide the crystal habit effect by an examination of the adsorption isothermals in dilute solution. If the ordinary isothermal were valid, i.e., $\alpha = ac^{\frac{1}{n}}$ (α = adsorption value, a = const. C = equilibrium concentration after adsorption, n = constant) then the relation between log α and log.c would be linear. If the types of lead styphnate were similar differing only in surface area then the log α /log c lines would be strictly parallel to one another for the various types of lead styphnate; i.e. the exponent $\frac{1}{n}$ should have the same value. Thus if it were found that the exponent $\frac{1}{n}$ were constant for the various types of lead styphnate it could be concluded that the difference in graphite incorporation was simply due to a difference in specific surface area and not to an inherent adsorption power of R.D.1303.

The quantity of gelatin added during the graphiting process ffects the specific resistance of the product to some extent, but the main difficulty due to the addition of an excess of gelatin would be caused by the aggregation of the product from which processing difficulties might arise.

Although the graphiting of R.D.1302 (sp. area 300-400 cm^2/g) directly after manufacture by the pretreatment method has given products with specific resistances comparable with a "non-static" lead styphnate in the loose state, it has not been possible to increase the graphite content much beyond the minimum graphite value (1.2 per cent). It is doubtful whether the graphiting of R.D.1302 could be considered as a satisfactory project for extension to the manufacturing scale in its present form, since there is a possibility of obtaining material with low graphite content and high specific resistances which is more sensitive to electric charges than the untreated lead styphnate (See Appendix VI). The graphite content and specific resistance in the region of specific areas 300-400 cm^2/g is critically dependent on the surface area of the lead styphnate.

TABLE V.

Graphiting S.12 RD.1302.

General:-

Lead Styphnate:-	RD.1302 S.12. 14 mls wet vol. = 20 gms dry wt.
Aquadag:-	Diluted Aquadag & graphite analysed 3.6% graphite.
Gelatin:-	1% solution. Commercial kibbled.
Apparatus:-	250 ml. tall beaker, s.s. stirrer, no baffle.

Procedure: Vol. of lead styphnate measured out wet, stirred with approximately 40 mls. water. Diluted Aquadag added and total volume made up to 100 ml. with water. Gelatin solution added slowly drop-wise with frequent examination of the material and occasional trial settings. Two water washings given, filtered and dried on 40-50°C hot table, then sieved 60 mesh in the usual manner. Temp. 18-20° except CG.67. All resistance measurements carried out using the Mullard Measuring Bridge.

Batch No.	Experimental	Aquadag 3.6% C		Gelatin Soln. 1%		Processing	Product	Anal. % C	Sp.Res. ohms x 10^4 per cm^3	Remarks
		Vol. used m/s	%C on L.S.	Vol. mls.	% on L.S.					
CG 63	Graphiting with 2% colloidal graphite and 0.35% gelatin addition.	11.2	2.0	7.0	0.35	4 ml gelatin:- Clear liquors but segregation. 6 mls gelatin:- No signs of segregation Some caking on drying.	Uniform dark brown some aggregation of cryst. Graphite patches on crystals.	1.72	21.4	Very uniform resistance measurements.
CG 64	1.5% graphite & 0.35% gelatin addition.	8.4	1.5	7.0	0.35	4 mls gelatin:- good settling no segregation. 7 mls added to compare with CG 63. Good processing	Similar to CG 63.	1.29	146.0	Note increase in resistance.
CG 65	1% graphite & 0.35% gelatin addition.	5.6	1.0	7.0	0.35	Graphite attached after 4 mls gelatin addition. Good processing.	Dark brown uniform colour. Increased aggregation of crystals.	0.75	640	Note the decrease of resistance with decrease in gelatin addition.

TABLE V. (Contd.)

Batch No.	Experimental	Aquadag 3.6% C		Gelatin Soln. 1%		Processing	Product	Anal. % C	Sp.Res. ohms x 10^4 per cm^3	Remarks
		Vol. used mls.	%C on L.S.	Vol. ls.	% on L.S.					
CG 66	Reduction in gelatin using 1% graphite.	5.6	1.0	3	0.15	No segregation after 3 mls gelatin addn. Very slight segregation in final wash. Good processing.	As CG 63 but very little aggregation.	0.75	640	Note the decrease of resistance with decrease in gelatin addition.
CG 67	Addition of 1.5% graphite with minimum gelatin.	8.4	1.5	5	0.25	Slight segregation after 4 mls gelatin no segregation after 5 mls gelatin some signs of segregation in the washes.	As CG 63 with little aggregation.	1.74	5.9	Note again the reduced resistance due to decrease in gelatin added.
CG 68 & CG 69	Attempt to incorporate 2% graphite using 0.25% gelatin	11.2	2.0	5	0.25	Segregation obvious after the 5 mls gelatin addition. Final wash with swirling showed complete segregation.	Discarded			Addition of 0.25% gelatin is insufficient to incorporate 2% colloidal graphite.

TABLE VI

Appendix III

General Conditions

Apparatus: 1 L squat beaker, anchor stirrer, stirring speed 200-300 r.p.m., vessel for lead acetate delivery in 52 secs. (4 mins. in CG.102).

Quantities:

Magnesium Styphnate 24/10/44	(123g. S.A/1 (40.8g.Mg.CO_3/1)	p.H 4.2	200 mls	Precipitation
Pb Ac_2 SH_2O	300 g/1		117.6 mls	
HNO_3	220 g/1		41.2 mls	
Lead Styphnate		1/3rd yield		Graphiting
Water		70 mls.		
Diluted Aquadag	4.2% C	7.2 mls.		
Gelatin 1% soln.	up to	5 mls.		

Procedure:- Mg. Styphnate stirred at 75°C. and lead acetate solution (heated to 75°C.) added in 52 secs. (4 mins. in CG 102), mixture stirred and maintained at 75°C. for the required time (basic salt stage), nitric acid run in at a constant rate during the time allowed. The charge stirred for 10 mins. after the nitric addn. cooled to 30°C. settled, decanted, and washed 2 x 300 mls. H_2O.

1/3 of the yield was suspended in water and stirred, the diluted aquadag added, followed by the slow addition of gelatin. The material was allowed to settle, decanted, and washed 2 x H_2O, dried and sieved 60 mesh.

Batch Date	Experimental	Basic Salt Stage		Nitric addition and Normal salt stage		Product	Graphiting		Remarks
		Time mins	Appearance at - mins.	Time mins			Temp. °C.	Processing	
CG 95 4/9/45	Long basic salt stage and rapid nitric acid addition.	19	Usual small aggregates up to 5 mins. 5 mins: start of larger aggregates 7 mins: first hair crystals 10 " increase in hair crystals. 12 " increased viscosity 15 " Columnar xals, no hairs, nuclei 19 " No aggregates. Mainly columnar but many nuclei.	½	1 min. after addn. N-salt growing from columnar crystals. 3 mins. no columnars but tendency to aggregation. 10 mins. No change.	Cluster aggregates variety of crystal sizes. Small crystals are tabular - Large crystals are thick but present a hexagonal profile. Aggregation.	20	Flocculation and slight segregation before addition of gelatin; after 2 mls. gelatin no segregation after 4 mls. gelatin no segregation.	Satisfactory processing. Increase in viscosity caused no stirring difficulty.

TABLE VI (contd.)

Batch Date	Experimental	Basic Salt Stage					Graphiting		
		Time mins	Appearance at - mins.	Time mins	Nitric addition and Normal salt stage	Product	Temp. °C.	Processing	Remarks
CG 96 6/9/45	Long basic stage and rapid nitric addition.	19	- ditto -	$3\frac{1}{2}$	During nitric addn. the nuclei first dissolved (1 min). At the end of the HNO_3 addn. N- salt growing from the columnars. All normal salt after further 1 min.	More uniform in size than CG 95, and less aggregation. Mainly orientated with hexagonal profile.	19	- ditto -	- ditto -
CG 97 7/9/45	Long basic stage slow nitric addition.	19	- ditto -	22	No nuclei after 5 mins. 15 mins. N-salt growing from columnars. 22 mins few needled which disappeared on stirring.	Practically no aggregation. Large clear crystals with enlarged basal plane Tabular habit presenting a hexagonal profile. Striations parallel to axis. Many liquid inclusions	20	Flocculation and segregation before gelatin addition up to 5 mls. added. Obvious segregation	Product did not graphite satisfactorily.
CG 98	Short basic stage rapid nitric addition.	4	2 mins: small aggregates 4 " " " few nuclei type cryst.	$2\frac{1}{2}$	2 mins. after nitric addition all normal salt.	Some aggregation. Thick equant type of crystal, mainly square profile. Many liquid inclusions. No striations.	19	Flocc. and seg. before gelatin. 1 mls. gelatin colour change to brown 4 mls. gelatin slight signs of segregation.	Note the formation of equant normal salt.

TABLE VI (contd.)

Batch Date	Experimental	Basic Salt Stage		Time mins	Nitric addition and Normal salt stage	Product	Graphiting		Remarks
		Time mins	Appearance at - mins.				Temp. oC.	Processing	
CG 99	Short basic stage Intermediate rate of nitric addn. (10 mins)	4	2 mins: small aggregates 4 " " " few nuclei type particles (No needles or hair crystals)	10	3 mins. addn. aggregates, hair crystals start of N-salt. 6 mins: all normal salt. No further change.	Some aggregation. Variation in crystal size. Equant type of crystal showing irregular hexagonal profile.	19	Flocc. and seg. before addn. of gelatin. After addn. of gelatin no segregation. Slight segregation in 2nd. wash.	
CG100	Short basic stage slow nitric addition.	4	2 mins: aggregates and fines (No needles) 4 mins: No change	20	3 mins: aggrs. and fines 6 " start of hair crystals 8 " all normal salt 8-20: No change.	Very little aggregation, equant type crystals. Similar to CG 99 liquid inclusions. Square profile.	19	Flocc. and seg. before gelatin addn. No seg. after addn. Slight segregation in washes.	
CG102 20/9/45	4 mins. addition Pb Ac_2. Short basic stage. Medium nitric addition.	6	0 mins: aggregates only 3 " " hair crysts. few H-salt. 6 " aggregates many hair crystals, N-salt.	7½	3 mins: agregates, hairs and N-salt. end of addn. All normal salt.	Mainly equant crystals some tabular type. Many unusual shaped inclusions.	21	Flocculation and segregation before gelatin addn. After 6 mls. gelatin, segregation obvious but some attachment of graphite clusters.	

Appendix III

TABLE VII

Precipitation and Graphiting of Lead Styphnate.

General

Magnesium Styphnate:- 184.8 g SA/1.) p.H 4.8 200mls.
6.55 g MgO/1)

Lead Acetate:- 315 g $PbAc_{2}3H_{2}O/1$ 168mls.

Nitric Acid:- 220 g $HNO_{3}/1$ ·78 mls.

Apparatus:- 1l squat beaker, anchor stirrer
revs. 200-300 r.p.m.

Graphiting:-
Lead styphnate :- $\frac{1}{3}$ ct
volume ≡ 15 g: water. 70 mls.
Colloidal graphite 3.35% C W/V
normally 11.2 mls. (increased
to 13.4 mls. for CG.121 and 123)

Procedure:- Mg. Styphnate stirred at 75°C. and lead acetate solution heated to 75°C. added in $1\frac{1}{2}$ mins. The mixture was stirred and maintained at 75°C. for the required time (basic stage), then nitric acid run in at a constant rate during the time allowed. The mixture stirred for 10 mins., cooled to 30°C., settled and washed by decantation. A known volume of the wet product (approx. 15 mls.) was dried and weighed. A volume equivalent to 15 g dry weight of the remainder of the wet batch was stirred in water, the colloidal graphite added followed by the slow addition of gelatin solution. The product was washed by decantation and dried in the usual manner. The product was sieved through 60#.

Batch	Experimental	Basic Salt Stage		Nitric acid additions and normal salt.		Product	Graphiting	Remarks
		Time (mins)	Appearance at - mins.	Time (mins)	Appearance			
CG. 121	10 minute basic stage; $\frac{1}{2}$ min. nitric addition.	10	0 Small aggregates 3 Start of fine needles 6 mixture of hair crystals needles and nuclei 9 Accicular crystals and nuclei.	$\frac{1}{2}$	At the end of nitric addn. normal salt crystals attached to the accicular basic salt. After 3 mins no accicular crystals present.	Much aggregation, many chain aggregates crystals mainly of tabular type.	Before addn. of the gelatin there was flocculation of the graphite, but the flocculi remained dispersed. After addition of gelatin the graphite became attached to the L.S.	

TABLE VIII (Contd.)

Basic	Experimental	Basic Salt Stage		Nitric acid additions and normal salt.		Product	Graphiting	Remarks
		Time (Mins)	Appearance at- mins.	Time (Mins)	Appearance			
CG.122	5 min. basic stage, 1 min nitric addition.	5	0 Usual small aggregates. 4 Mixture of aggregates and hair crystals.	1	Small clear equant crystals first appear followed by large equant type.	Many large opaque equant crystals with small crystals adhering.	Some graphite becomes attached after gelatin addition; major portion removed in washes.	The reduction time of basic stage gives large crystals even with rapid nitric addition.
CG 123	10 min. basic stage 5 mins. nitric addition	10	0 Smallaggregates 6 Hair crystals and eggs. 9 Acicular and nuclei crystals 10 As 9 mins.	$5\frac{1}{2}$	Nuclei disappear after $\frac{1}{2}$ vol. HNO_3 and bladed crystals of various size form. Normal salt form on the bladed crystals.	Aggregates, poor crystal forms. Mixture of tabular and equant crystals.	Graphite flocculated but remained dispersed in liquor before gelatin addn. After gelatin addition good attachment of graphite.	Proportion of graphite added increased to 3.0% because of the large surface area.
CG.124	10 mins. basic stage; 17 mins. nitric addition.	10	Similar to CG.123	17	3-6 long and short bladed cryst. 9 As 3-6 with few N-salt 12 Mainly large equant type N-salt some bladed cryst. still present. 15 all N-salt.	Various size crystals, mainly tabular with a few large equant crystals.	Flocculation and segregation before gelatin addn. Fair attachment after gelatin addition some graphite removed in washes.	

Appendix III

TABLE VIII

GENERAL

Bulk density:- Is apparent bulk density in butyl alcohol using lead Azide B.D. tube.

Sp. surface area:- Measured by air permeability method.

Average particle size:- Measured by Martin's diameter average of 200 crystals taken. Class size measured from 0.015 m.m. by intervals of .01 m.m.

p.H. of M.L. from graphiting measured by glass electrode.

Specific resistance:- Measured by method of Appendix No. Figures in ( ) represent repeat experiments. (V) indicates a variable result for specific resistance determinations.

Batch No.	Experimental	Wet Vol (mls)	Calc. yield (grms)	B.D. (Butyl-alcohol) (g/ml	Sp. Surface Area (cms^2/g)	Average particle size (m.m.)	Particle size distribution % in class sizes (m.m.)				M.L. p.H.	Graphite content C.	Sp. Resist. (x10^{4}ohms/cm^3)	Remarks
							.025	.025-.045	.045-.055	.055				
CG 95	Mg.Styphnate as Table VI Long basic salt stage. Rapid nitric addition	42	34	1.07	1,050	.0155	91	8.5	0.5	0	5.94	2.53	18	
CG 96	Mg.Styphnate Table VI. Long basic stage Rapid nitric addn.	42	34	0.9	1,040	.0206	73	24	2	1	5.82 (6.12)	2.14 (2.68)	870 (V) (11.7)	The small particle size crystals require higher minimum graphite content.
CG 97	Mg.Styphnate Table VI. Long Basic stage slow nitric addn.	32	36	1.02	586	.0367	27.5	43.5	15.5	13.5	6.00 (6.12)	1.08 (0.725)	11,000 (11,000)	Note high pH value and low graphite content.
CG 98	Mg.Styphnate Table VI. Short basic stage, rapid nitric addition.	34	26.01	1.25	712	.02	78.5	21.5	0	0	5.92	1.85	61	This graphite content is near the minimum value
CG 99	Mg.Styphnate Table VI. Short basic stage. Medium nitric addition.	33	29.1	1.22	695 (697)	.0235	63.5	29.5	5.5	1.5	5.98	2.3	37	The increase in time of addition of nitric acid has made little difference in the surface area c.f. CG 98

TABLE VIII (contd.)

CG 100	Mg.Styphnate Table VI. Short basic stage, slow nitric addition.	30.5	28.7	1.39	537	.0305	44	41	8	7	5.9 (6.14)	1.74 (0.74)	72 (V) (14,000)	
CG 102	Mg.Styphnate Table VI. 4 min Pb AC_2 addn. Short basic stage; medium nitric addition.	23	40	1.57	305 (294)	.0388	36	32	8.5	23.5	6.0	0.24	11,000	
CG 121	Mg.Styphnate Table VII. 10 min basic stage. Rapid nitric addition.	36	60.7	1.10	1,014	.0166	88	12	0	0	5.58	3.24	23.2	
CG 122	Mg.Styphnate Table VII. 5 min basic stage. Rapid nitric addition.	37.8	57.2	1.42	384	.0336	44.5	33	7	15.5	5.82	-	11,000	Explodes using 500 V Megger. Reduction of basic stage has given large crystals of lead styphnate even when the nitric acid is added rapidly.
CG 123	Mg.Styphnate Table VII. 10 min basic stage, medium nitric addition.	38	63.4	1.12	1.184	.0144	95	5	0	0	5.9	3.16	1.86	
CG 124	Mg.Styphnate Table VII. 10 min basic stage; slow nitric addition.	38.8	54.6	1.47	534	.0342	30.5	48.0	12.0	9.5	5.92	1.5	70 (V)	

APPENDIX IV

Graphite Wet Mixing Processes

It has been shown earlier that incorporations of graphite up to 13.7 per cent from dispersions of colloidal graphite in organic solvents have not given material satisfactory for the 20 mm. electric cap, unless additional powdered graphite has been added. A method for the incorporation of sufficient powdered graphite with R.D.1303 to give a suitable cap composition would be a considerable advance in technique. This investigation has been divided into two portions.

A. The incorporation of powdered graphite with R.D.1303 by a wet mixing method.

B. The incorporation of both colloidal and powdered graphite with R.D.1303.

A. Wet mixing process for R.D.1303 and 10-12 per cent. powdered graphite

The experimental work and procedure are detailed in Table IX. The powdered graphite used in these experiments was Acheson's 35 of specific surface area 5,910 cm^2/g; this material has been found suitable for the dry mixing process. Some difficulty was experienced in wetting the powdered graphite in early experiments (CG.27) and it was found necessary to employ a wetting agent.

The process is a modification of the Aquadag graphiting process except that a suspension of powdered graphite was substituted for the colloidal graphite. In CG.28, the addition of 1% gelatin solution, equivalent to 0.2 per cent. gelatine (calc. on R.D.1303), to the R.D.1303/graphite suspension, gave some indication of graphite segregation on washing. A standard procedure was adopted to determine if segregation occurred in the wet state; after allowing the mixture to settle, it was given a gentle swirling motion by hand, any tendency for segregation was shown by the appearance of a thin black ring of graphite.

No segregation was observed in CG.32 and CG.33 where 10 per cent. graphite was readily incorporated using 1.0 and 0.6 per cent. gelatin respectively. Although slight segregation was noted in CG.28, where 0.2 per cent gelatin was used as the incorporating agent, the final product processed well to give a deep yellow, free flowing material with no signs of segregation in dry state.

An increase in graphite content to 12.5 per cent. required the addition of 0.6 per cent. gelatin to give a non-segregating type of product (CG.34); the use of only 0.4 per cent. gelatin gave segregation in the wet state, although processing was good and the dried product showed no indication of graphite segregation (CG.35).

During attempts to reduce the quantity of gelatin necessary to give a non-segregating product, the addition of tannic acid as a gelatin precipitant was tried. The addition of 0.4 per cent. tannic acid to the mixture as in CG.29, containing 0.2 per cent. gelatin showed slight segregation in the wet state and the final product showed greater aggregation than CG.28 in which 0.2 per cent gelatin had been used without tannic acid addition. An increase of tannic acid to 1.0 per cent. (CG.30) caused the precipitation of a fibrous material (gelatin tannic complex) and although no segregation was observed the final product was very aggregated. The addition of ammonia before the addition of tannic acid (CG.31) gave a poor type of product for processing; 0.07 per cent. ammonium hydroxide causing the mixture to become dispersed in the liquor and remaining stable for a considerable time before settling out occurred. It appeared that no useful purpose was served by the addition of tannic acid or ammonia.

The values of the specific resistances of the series CG.28 - 35 reported in Table IX show a great difference for the materials incorporating 9.2 per cent graphite and those incorporating 12.5 per cent. The former have high resistances ($> 100 \times 10^6$ ohms/cm.^{3}) while the latter have values as low as 13×10^4 ohms/cm.^{3}. Lead styphnate having high specific resistances may be considered to be as sensitive to static charges as the ordinary dry mixed R.D.1303/graphite composition, (see A.R.D. Explosives Report No.281/45). Products containing 12.5 per cent. graphite (CG.34 and 35) of low specific resistance would have a low order of static risk. (C.f. CG.19 Appendix I).

During determinations of specific resistances using the 500V Megger, it was noted that all the materials containing 9.2 per cent. graphite detonated readily while products containing 12.5 per cent. graphite did not.

Four batches of the series were tested for the 20 mm. electric cap (see Table IX) and it was shown that products containing 9.2 per cent. graphite were unsatisfactory because of their high firing resistances, but products containing 12.5 per cent. graphite functioned satisfactorily in the cap test. There was some difference in the firing resistances of the two batches CG.34 and CG.35 although their firing voltages were well within the specific limits; the difference was probably due to the difference in gelatin content of the two products. It was observed again that where some excess of gelatin has been employed the product tends to become aggregated.

B. Combination Process Incorporation of Powdered and Colloidal graphite by a wet process.

Although the wet mixing process above has shown that the incorporation of 12.5 per cent. graphite will give a material suitable for the 20 mm. electric cap and that it has a low static risk in the loose state, the material showed many free styphnate crystals (see fig.19); a reduction of the graphite content would probably lead to a static sensitive material being prepared. A preliminary graphiting with colloidal graphite to incorporate approximately 2.5 per cent. graphite followed by a wet mix with powdered graphite would give a "non-static" product which was independent of the powdered graphite content.

A number of 20 grm. scale preparations showed that, after graphiting R.D.1303 with colloidal graphite using gelatin as the incorporating agent, the subsequent addition of a suspension of powdered graphite in water gave a clear supernatant liquor on settling, but that the particles of powdered graphite were not attached to the lead styphnate. The subsequent addition of gelatin solution caused the particles of powdered graphite to become attached to the graphited R.D.1303. The process may be considered as a combination of the graphiting process described in Appendix I and the wet mixing process described above. The specific resistance values of the products were low and comparable with a "non-static" lead styphnate and in view of the satisfactory incorporation and the possible extention to the plant scale, the preparation of a 5 oz. laboratory batch is described in detail :-

Combination Process on the 5 oz. scale

Quantities

		per 100 grms. R.D.1303
Stage A. (Colloidal Graphiting)		
R.D.1303 S.23	82 mls. (≡ 130 g.dry)	100
Colloidal graphite 3.6% C (W/V)	81 mls.	2.5 grms. graphite
Water made up to	500 mls.	
Gelatin 1% solution	23.2	0.2 grms. gelatin
Stage B (Wet mixing)		
(Powdered graphite Acheson's 35	13.5 g.	11.25 grms.
(Water	30 mls.	
(Johnson's 326 Wetting Agent	2 mls.	
Gelatin 1% solution	35 mls.	0.3 grms.

Procedure

Stage A The R.D.1303 was measured out wet and suspended in approximately 200 mls. of water, the colloidal graphite suspension obtained by diluting 'Aquadag' was added while the mixture was being stirred, the volume was made up to 500 mls. with water. The mixture was stirred and the gelatin solution added during 10 minutes at room temperature (18-20°C).

Stage B After stirring for a further 5 minutes the suspension of powdered graphite in water containing the wetting agent was added, followed by the addition of gelatin solution during 13 minutes. The mixture was allowed to stir for a further 5 minutes, settle for 5 minutes, and the mother liquor decanted off. The product after washing twice with water and once with alcohol was dried at 40 - 50°C. then sieved through 60 mesh.

Process Remarks

Completion of stage A was indicated by a trial settling after the gelatin addition; a clear liquor with rapid settling, no segregation and attachment of graphite indicates a satisfactory preliminary graphiting.

During Stage B, after the addition of 25 mls. of gelatin solution a trial settling showed cloudy liquors and some signs of segregation on gentle swirling after the addition of 35 mls. of the gelatin solution, the liquor settled rapidly giving a clear supernatant liquor with no signs of segregation of the product on gentle swirling. Washing by decantation was rapid.

Product:- Consisted of dark coloured free flowing material with some small aggregates (see fig.20).

Graphite Content:- 12.1 per cent. graphite
Specific Resistance (Loose powder) 2.8 x 10^4 ohms/cm^3
Electric Cap Test

Pressing load 1,000 lb. Firing Resistance 7.0 ohms.
Firing voltage 11.0 volts

Conclusions and Discussion

It has been shown that powdered graphite can be attached to R.D.1303 in a manner similar to that used for the attachment of graphite flocculi obtained from a colloidal graphite suspension.

A distribution of 9.2 per cent. of the particular graphite used i.e. Achesons 35 Sp Area 5,910 cm^2/g, resulted in a product having a greater sensitiveness to electrostatic charges than the untreated R.D.1303. When the distribution of powdered graphite was increased to 12 per cent. of the mixture, the product had a specific resistance comparable with a non-static lead styphnate. It appears that a certain distribution of graphite is necessary to give the required graphite to graphite contacts to ensure a material with low specific resistance, the distribution required depending on the particle size of the graphite other factors being constant. As indicated previously, a minimum graphite distribution value can be determined below which value the product will have a high specific resistance in the loose state and a low energy of electrical ignition.

The minimum graphite distribution is also dependent on the particle size or surface area of the lead styphnate, but considering R.D.1303 which has a specific surface area of approximately 700 cm.^{2}/g the minimum distribution value for graphite of surface area 6,000 cm.^{2}/g is of the order of 10 - 11 per cent. graphite, while graphite flocculi obtained from colloidal graphite i.e. having an extremely large surface area, the minimum value would be approximately 1.8 per cent. graphite.

During specific resistance measurements using the 500V Megger, all the wet mixed products containing 9.2 per cent. graphite detonated, whereas with determinations with products containing 12 per cent. graphite, no detonations occurred. This difference must be due to the different electrical leakage values of the materials.

A preliminary graphiting of the R.D.1303 by the colloidal graphite method, followed by a wet mixing procedure has given a product which fires within the proposed acceptance range for the 20 mm. cap composition. In the loose state the specific resistance of the material indicated that the electrification risk is lower even than CG.19 (QV). Increased scale preparations from 20 grm. to 5 oz. has shown good reproduction of the essential properties.

A comparison of the four types of compositions which have been found to fire satisfactorily in the 20 mm. electric cap test, is of interest, their chief characteristics are tabulated below :-

Composition	Method used	Specific Res. ohms. x 10^4	Detonations with 500V Megger
R.D.1303 + 12.5% powdered graphite	Dry Mixing	$>$10,000	Detonations
R.D.1303 + 12.5% powdered graphite	Wet mixing	19	No detonations
R.D.1303 + 2.5% graphite from colloidal graphite + 10% powdered graphite	Wet combination process	2.8	No detonations
Graphite R.D.1303 + 8.8% powdered graphite	Dry mixing	0.43	No detonations

A comparison of the products obtained from the R.D.1303/graphite dry and wet mixing processes show that they have a similar appearance under the microscope i.e. they consist of an intimate mixture of lead styphnate crystals and graphite particles (C.f. fig. 6 and 9). The wet mixed material however, gives a low specific resistance in the loose state compared with that of the material obtained by the dry mix process. Also the wet mixed material does not detonate in the 500V Megger test. The products from the combination process and the graphited R.D.1303 powdered graphite dry mixing process, both show that each crystal of styphnate is graphited and the particles of powdered graphite are attached to the lead styphnate crystals. (See figs. 19 and 4).

Of the four compositions tabulated above it would appear that the most satisfactory type of product from the manufacturing point of view would be that prepared by the combination process. The process would follow directly after the manufacture of the R.D.1303 and obviate a dry mixing procedure. The dry mixing of graphited R.D.1303 and powdered graphite would offer no electro-static risks, but the mixing process would be limited to 8 oz. batches with the existing type of equipment.

TABLE IX Wet Mixing 10 - 12.5% Graphite and RD.1303.

General

RD.1303 Lead Styphnate:- RD.1303 Lot S.24, 9 lb. batch RD. manufacture at Swynnerton. Wet Vol. 14.5 mls. = 20 grms. dry weight.

Procedure.

S.24 measured out by wet volume and stirred in approx. 50 mls. water. Powdered graphite hand stirred into approx. 20 mls. water containing 3 drops 326 Johnson's wetting solution (Not CG27). The graphite suspension was added to the RD.1303 suspension and washed in with water to bring the total volume to 100 mls. 1% gelatin solution was added in approx. 2 minutes. Temp. 18-20°C. Mixture stirred further 2-5 minutes, washed and dried in the usual manner. Sieved 100 mesh.

Batch Date /45	Experimental	Graphite Acheson's 35		Gelatin		Processing	Product	Sp.Res. ohms./cm^3.	Graphite by Analysis %	20 mm. Cap Test		
		Wt. grms.	% Calc. on Product	1% Soln. Vol. mls.	% Calc. on Lead Styphnate					Pressed Resistance ohms.	Firing Volts volts.	
CG27 9/1	We mixing 10% graphite using 0.2% gelatin.	2	9.2	4	0.2	Powdered graphite floated on the surface and wetting difficult. Alcohol added but not very satisfactory. Good settling no segregation.	No segregation of graphite in the dry state. Deep yellow free flowing material.	-	-	-	-	Alcohol unsatisfactory for wetting graphite
CG28 9/1	Repeat CG27 using wetting agent with the graphite.	2	9.2	4	0.2	Graphite wetted with Johnson's 326. Slight segregation of graphite in the wet state after swirling. Good sieving etc.	As for CG27	100 x 10^6	-	250	14	Detonation when using 500V. Megger for resistance measurements. Johnson's 326 satisfactory for wetting agent.

TABLE IX Contd.

Batch		Graphite Acheson's 35		Gelatin						20 mm. Cap Test		
Date /45	Experimental	Wt. grms.	% Calc. on Product.	1% Soln. Vol. mls.	% Calc. on Lead Styphnate	Processing	Product	Sp.Res. ohms./cm^3.	Graphite by Analysis %	Pressed Resistance ohms.	Firing Volts volts.	
CG29 10/1	Addition of 4% tannic acid to gelatin, RD.1303 graphite suspension in water.	2	9.2	4	0.2	4 mls. 2% Tannic acid solution added slight segregation on gentle swirling. Good sieving etc.	No signs of segregation in the dry state. A few large aggregates of RD.1303 and graphite.	>100 x 10^6	-	-	-	Aggregates smaller than 100 No over size on sieve. Detonations using 500V. Megger.
CG30 11/1	Addition of 1% tannic acid to gelatin, RD.1303 and graphite suspension.	2	9.2	4	0.2	4 mls. 5% tannic acid solution added, slide showed presence of elongated fibrous material. Appears to be no segregation good processing.	Similar to CG29 but with an increase in the number of aggregates.	100 x 10^6	9.2	-	-	Poor type of product, too many large aggregates.
CG31 11/1	Ammonia added to gelatin, RD.1303 and graphite suspension before addition of 1% tannic acid.	2	9.2	4	0.2	4 mls. $\frac{N}{10}$ Am OH added. After tannic acid (4 mls. 5%) addition no settling; 1303 and graphite dispersed. Destroyed.	Destroyed	-	-	-	-	

TABLE IX Contd.

Batch		Graphite Acheson's 35		Gelatin						20 mm. Cap Test		
Date /45	Experimental	Wt. grms.	% Calc. on Product.	1% Soln. Vol. mls.	% Calc. on Lead Styphnate	Processing	Product	Sp.Res. ohms./ cm^3	Graphite by Analysis %	Pressed Resistance ohms.	Firing Volts volts.	
CG 12/1	Wet mixing of 10% graphite using 1% gelatin	2	9.2	20	1.0	No signs of segregation. Cakes on drying and gives poor sieving due to caking.	Free flowing no segregation of graphite. Some aggregates of RD.1303 and graphite.	100×10^6	-			The caking on drying may be due to inefficient alcohol washing. Detonations with 500V. Megger.
CG33 12/1	Wet mixing 10% graphite using 0.6% gelatin.	2	9.2	12	0.6	As for CG32 but breaks up easily after drying.	Some aggregates but most of the graphite is attached to the RD.1303.	100×10^6	-	100	18	The alcohol washing here was stirred with the wet product no difficulty in sieving.
CG34 16/1	Wet mixing of 12½% graphite (on product) using 0.6% gelatin	2.86	12.5	12	0.6	No segregation. Breaks up well on drying. Good sieving.	Mos of the graphite is attached to the RD.1303	13×10^4	-	18	11	Satisfactory product note the low electrical resistance in loose state C.f. CG.19.
CG35	12½% graphite using 0.4% gelatin.	2.86	12.5	8	0.4	Some indication of slight segregation after the alcohol washings. Good processing.	Similar to CG34	19×10^4	12.6	.8	10	Material satisfactory for cap firing.

Appendix V

The Wet Incorporation of Aluminium Powder and Aluminium Stearate with R.D.1303

The previous Appendices have detailed the incorporation of graphite in its various forms as a conducting material; consideration of compatibility etc. of other conducting materials indicated that the incorporation of aluminium powder with R.D.1303 might act in a manner similar to that of the products from the graphiting processes. In addition it was considered possible that the incorporation of an inert material, e.g. aluminium stearate, although a non-conductor, would have practical application in giving effective lubrication during filling and pressing procedures thus contributing to the safety of such operation.

Incorporation of Aluminium Powder with R.D.1303

A large variety of commercial aluminium powders are available and for a number of samples the values for specific surface area and resistance were determined. The finest type of aluminium powder (Sp. Area 6, 225 cm^2/g) had a specific resistance ($> 14 \times 10^7$ $ohms/cm^3$) which was attributed to the presence of an oxide film over the surface of the aluminium particles. Other grades of aluminium powder were available which, although of smaller surface area, had specific resistances comparable with that of the graphite powder used in previous work. A selection of four grades of powder was made for the investigation and their characteristics are detailed with the experimental work in Table X.

The experimental procedure was similar in each experiment, the aluminium being wetted with the gelatin solution and the mixture washed into the lead styphnate suspension, to the stirred mixture was then slowly added a solution of tannic acid.

The Bag House dust (A.S.1 and A.S.2) represents the finest commercial powder available but the particles are probably well coated with an oxide film, incorporation of this powder as in A.S.1 and A.S.2 showed no segregation and the processing of each batch was good. The final products showed some unattached particles of aluminium powder to be present (Fig.21); the products also gave high values for specific resistance measurements. The fine powder used in these two experiments showed some initial reactivity when wetted with water; for this reason and also presence of the oxide film, coarser types of aluminium were used which had low specific resistance values.

The incorporation of aluminium powder with surface area 950 cm^2/g. having a specific resistance of 30 $ohms/cm.^3$ (A.S.3) showed some signs of segregation in the wet state even after the addition of up to 1% tannic acid (calc. on R.D.1303). Processing, however, was satisfactory and no segregation was observed in the dry state. The product consisted of a free flowing, light yellow material which under the microscope showed some unattached aluminium particles, these can be seen in Fig.22 as bright elongated particles. No initial reaction was noted when the aluminium powder was wetted, the material however is probably too coarse to give satisfactory incorporation. Although the incorporated aluminium had a low specific resistance the final product of a 10% incorporation had a high specific resistance.

The two samples used in A.S.4 and A.S.5 had specific surface areas of 1140 and 1350 cm^2/g. respectively and also low specific resistances (34 and 16 $ohms/cm^3$)

Both samples incorporated well without the need for adding tannic acid solution; the tannic acid solution was added, however, in order to keep conditions constant. The products were similar in both cases and the aluminium was incorporated mainly on the aggregates of lead styphnate which showed a bright metallic surface (Fig.23).

In previous work the incorporation of powdered graphite has required a certain minimum distribution in order to give a conducting product, the distribution depending on the size of conducting particle, other things being constant. In experiments A.S.4.A. and A.S.4.B., 15 and 20 per cent aluminium powder has been incorporated by the addition of only 0.1 per cent tannic acid. The addition of tannic acid was necessary with these quantities of aluminium to give clear mother liquors. Both products were shown to have high values of specific resistance and the product containing 20 per cent aluminium powder gave one detonation out of six trials using the 500 V. Megger.

Incorporation of Aluminium Stearate

Concurrently with the investigation of a "non-static" lead styphnate, the incorporation of aluminium stearate with lead styphnate was tried as a means of obtaining a lead styphnate composition which would reduce the number of press fires in filling operations. The investigation is included in this report since the preliminary methods were based on the processes detailed in other Appendices.

A variety of methods were tried in order to incorporate 10 per cent of a sample of finely divided aluminium stearate powder with R.D.1303, but in each case the aluminium stearate segregated almost completely.

The idea of incorporating aluminium stearate in powder form was soon abandoned in favour of a method for incorporating aluminium stearate formed by metathesis in the presence of the R.D.1303.

The experimental work is tabulated in Table XI, the main variant being the method of precipitating the aluminium stearate. For the purpose of calculating quantities of solution etc. a slight excess of aluminium nitrate solution has been used to precipitate a product with a composition of $Al\ (CH_3(CH_2)_{16}COO)_3$ it is probable that the precipitate is a basic salt of aluminium stearate but no analyses are available to check this.

Use of Sodium Stearate

The addition of aluminium nitrate solution to the water suspension of lead styphnate (R.D.1303) stirred at 30°C. followed by the addition of a suspension of sodium stearate in hot water (D.S.7), caused the segregation of a very fine white precipitate, and the product remained unchanged after the addition of gelatin and tannic acid solutions.

The addition of sodium stearate to the hot suspension of R.D.1303 and subsequent addition of aluminium nitrate solution (D.S.6 and 12), gave a good processing type of product with no signs of segregation in the wet or dry state. In bulk the product was a pale yellow powder but under the microscope, the small aggregates consisted of yellow and white granules, together with many separate white granules (Fig.24).

Use of Stearic Acid

Another method for the precipitation of aluminium stearate was by the use of stearic acid (M.P. 69°C). In D.S.8 the stearic acid was added in alcoholic solution to the suspension of R.D.1303 stirred at 55°C. followedby the addition o aluminium nitrate solution. The resulting product consisted of a large soft spherical type granular material showing some light coloured patches on the individual granules (Fig.25). The addition of solid stearic acid to the hot water suspension of R.D.1303 gave a product consisting of a mixture of the large spherical granules and fine dusty material D.S.11). By adding aluminiu nitrate solution to the R.D.1303 suspension and the subsequent addition of stearic solution in alcohol (D.S.17) a small uniform granular type of product can be obtained, these individual granules also show white patches under the microscope.

Summary and Discussion

Certain types of aluminium powder can be incorporated in R.D.1303 up to 20% of the product without segregation. From previous experience it is probable that aluminium powder with a surface area greater than 950 cm^2/g. will incorporate satisfactorily with R.D.1303 but powder of smaller surface area tends to segregate in the wet state. Aluminium powders with a specific surface area of the order 6,200 cm^2/g. are very reactive in contact with water and usually have a high oxide content which causes the material to have specific resistances of a high order; aluminium powders of intermediate surface areas, while showing practically no reactivity with water, have low specific fesistances in the loose state and incorporate well with R.D.1303.

In spite of the low resistance of some of the aluminium powders it has not been possible to obtain a conducting composition by the incorporation of up to 20% of the powder in R.D.1303. It is possible that 20% aluminium is below the minimum distribution value or the aluminium surface becomes coated with a non-conducting film; in either case the product is of no use as a conducting composition or as a lead styphnate composition of reduced static risk.

The process for incorporation of aluminium powder might find practical application for use in mixtures such as A.S.A. etc. where aluminium powder is mixed in the dry state, which is a hazardous procedure due to the presence of aluminium dust.

It has been found difficult to incorporate powdered aluminium stearate with R.D.1303 by the wet process; by metathesis, compositions of a variety of physical forms have been obtained containing up to 10% aluminium stearate. No results of tests are available but a recent patent indicates the advantages of using aluminium stearate with initiators.

Appendix V

TABLE X

Incorporation of Aluminium Powder with R.D.1303

General Conditions:-

R.D.1303 Lead Styphnate:- BS50 used for A.S.1 and 2. Lot S.24 used for A.S.3 - 5. Materials used wet, volume measured equivalent to 20g. dry weight.

Gelatin solution:- 1 grm. commercial gelatin made up in 100 mls. water.

Aluminium:- Various samples. Surface areas determined by air permeability method.

Procedure:- The aluminium powder and gelatin solution were mixed and added to a suspension of R.D.1303 stirred in 60 mls. water. The total volume was made up to 100 mls. and a solution of 2% tannic acid added slowly. The mixture was allowed to stir for 5 minutes at laboratory temperature. After settling and decanting the material was washed twice with water and once with meths. in the usual manner, filtered and dried at 40-50°C. Sieved through 100 mesh.

Quantities:-

R.D.1303 volume	≡ 20 grms.
Water	60 mls.
Gelatin solution (≡ 0.5% on L.S.)	10 mls.

Aluminium as in Table.

Total volume made up to 100 mls.

Tannic acid 2% soln. as in Table.

Batch	Expt.	Lead Styphnate RD.1303 Wet Vol. (mls.)	Aluminium Powder			Tannic Acid				Processing	Product	Remarks
			Type	Sp. Surface Area (cm²/g)	Sp. Res. ohms/cm³	Wt. (grms)	% on R.D. 1303	Vol. (mls)	% on R.D. 1303			
A.S.1	Tannic acid added to Al/gelatin R.D. 1303 mixture	18.6 (BS50)	N.A.C. Bag-house Dust	6225	14×10^7	1	5	6	0.6	Rapid settling and clear liquors good sieving. No segregation.	Free flowing light yellow. Slight aggregation of L.S. No segregation of Al. powder.	Some reaction of the aluminium with water. Product has a high electrical resistance.
A.S.2	Aluminium content increased to 10%	"	"	"	"	2	10	4.5	0.4	Aluminium wetted with gelatin solution. No segregation with reduced quantity of tannic acid. Good processing.	Uniform colour free flowing many unattached small aluminium particles.	Product has high electrical resistance.

Table X (Contd.)

A.S.3	Use of coarser type of aluminium powder with low specific resistance.	14.5 (S24)	Cardiff Lot Car 998	950	3	2	10	10	10	Some signs of segregation in the wet state. Processing good.	Free flowing light yellow. Some bright particles also aggregates of LS/Al.	Segregation in the wet state. Product has a high sp. resistance.
A.S.4	Incorporation of intermediate type aluminium of low specific resistance.	"	N.A.C. Lot VI	1140	34	2	10	3	0.3	There were no signs of segregation after addition of Al/gelatin. Tannic acid stopped at 3 mls. Good processing.	Free flowing Al. incorporated in aggregation of RD.1303. Greater aggregation than usual.	There appears to be no nned for tannic acid. High electrical resistance.
A.S.5	Incorporation of 10% Aluminium powder containing 4% Cu of low specific resistance.	"	H.E.N. 121 (4% Cu)	1350	16	"	"	"	"	No segregation before tannic acid addition similar to A.S.4.	Similar to A.S.4.	Product had a high specific resistance.
A.S.4A	Incorporation of 15% Aluminium powder.	"	N.A.C. Lot VI.	1140	34	3	15	1	0.1	Some segregation before addition of tannic acid and mother liquors cloudy. 1 ml. sufficient to clear liquors. No segregation.	Slight aggregation most Al. attached. Bright surfaces on Al. particles.	High specific resistance
A.S.4B	Incorporation 20% Aluminium powder.	"	"	"	"	4	20	"	"	Ditto.	Slight aggregation good distribution. Bright surfaces on Al. particles.	" Detonated on the 500 V. Megger Test.

TABLE XI

Incorporation of Aluminium Stearate

eneral Conditions

Lead styphnate:- R.D.1303 Batch S.30. 20 grms. used.
Solutions:- 2% Tannic Acid in water. 1% gelatin in water. $Al\ (NO_3)\ 9H_2O$. 8.6 g/100mls. water. Stearic acid in 50% alcohol.

Procedure:- Lead styphnate (20 g.) suspended in water and stearate or aluminium nitrate added is detailed in "Experimental". Final solution added slowly (5 mins.) then stirred further 10 mins. ML decanted after settling, washed twice with water, once with alcohol. Dired 30 - 40°C. sieved 60 mesh except where stated.

Apparatus

250 ml. squat beaker
1.1/2" butterfly stirrer.
300 r.p.m.

Lot No.	Experimental	Stearate		Al. Nitrate soln. (mls.)	Al. stearate per 100 g. L.S.	Temp. (°C.)	Process Remarks	Product (a) Bulk (b) Micro examin.	Bulk Density		Remarks
		Type	Wt. (grms.)						Butyl Alcohol (g/ml.)	Scoop (g/ml.)	
D.S.6	Al.nitrate added to L.S. and stearate in 100 mls. water at 55°C.	Na.	2.1	15	10	55 (70)	Viscous at 55° temp. raised to 70 C. L.S. becomes attached to white granules. Free crystals. Processing good.	(a) Pale yellow fine. (b) Aggregation, many separate white granules	*	0.62	* Fine white material segregated in Butyl alcohol. Excess of Al. nitrate used.
D.S.7	Stearate in 100 mls. hot water added to L.S. + Al. nitrate. 10 mls. gelatin, then 3 mls. tannic acid soln. finally added.	"	"	10	"	30	Product bulky. High viscosity. Segregation of fine white layer. No change on addition of gelatin and tannic acid.	Segregation			Destroyed

TABLE XI

Lot No.	Experimental	Stearate		Al. Nitrate soln.	Al. stearate per 100 g. L.S.	Temp.	Process Remarks	Product (a) Bulk (b) Micro examin.	Bulk Density		Remarks
		Type	Wt. (grms.)	(mls.)		(°C.)			Butyl Alcohol (g/ml.)	Scoop (g/ml.)	
D.S.8	Al.nitrate added to LS. + stearic in 50% alcohol. (100 mls. water added with rapid stirring at end)	Stearic Acid in Alcohol.	1.95	10	"	30 (55)	30°C. aggregates and pale yellow silky material. At 55°C. and addition of water, aggregates. Good processing.	(a) Large shperical light yellow granules. (b) Smooth surface some light yellow patches.	0.83	0.78	Unusual type product. Granules qui soft.
D.S.9	Stearic acid soln." added to L.S. + Al. nitrate, Gelatin and tannic acid solutions finally added.		"	"	"	20 (70)	<u>20°C.</u>:- Slight aggregation no change on adding gelatin and tannic acid. <u>70°C.</u>:- Large aggregates formed.	(a) Uniform fine yellow. (b) Similar to R.D.1303 S.30	1.22	1.01	There is litt change in the R.D.1303. Cf. Bd. (butyl) RD.1303 = 1.25 g/ml.
D.S.10	Stearic acid soln. added to L.S. + Al. nitrate. Temp. 60°C.	"	"	"	"	60	Some aggregation. Good settling. Processing good.	(a) As D.S.9. (b) Some aggregates containing white particles.	1.06	0.85	Sample forwarded to Chorley for test 8.8.45.
D.S.11	Al.nitrate added to L.S. + solid stearic acid at 65°C.	Stearic Acid Solid.	"	"	"	65	Granulation, large rounded granules. High proportion of loose crystals good settling etc.	(a) Mixture of granules and fines. (b) Granules of L.S. with white patches Separate R.D.1303 and white particles	1.15	0.88	

TABLE XI

Lot No.	Experimental	Stearate		Al. Nitrate soln. (mls.)	Al. Stearate per 100 g. L.S.	Temp. (°C)	Process Remarks	Product (a) Bulk (b) Micro examin.	Bulk Density		Remarks
		Type	Wt.						Butyl Alcohol (g/ml.)	Scoop (g/ml.)	
D.S.12	Al.nitrate diluted to 50 mls. added to L.S. and solid sodium stearate at 65°C.	Na Stearate solid.	2.1	10	10	65	Mixture of aggregates and granules no change on adding Al. nitrate.	(a) Light fine. (b) Mixture of yellow and white granules of similar size.	0.69	0.6	This procedure has reduced the B.D. considerably.
D.S.13	Alcoholic stearic acid solution added to susp. of LS and Al. nitrate.	Stearic Acid. Soln.	0.975	5	5	"	Size of aggregates increases with stearic addition. Large aggregates in the hot. ML. turbid.	(a) Uniform colour fine material. (b) Very little aggregation.	1.08	0.88	Sample sent for test 8.8.45
D.S.14	Al.nitrate solution diluted to 50 mls. added to L.S. and solid stearic acid.susp.	Solid Stearic acid.	"	"	"	"	Large aggregates formed and some loose crystals in the hot.	(a) Mainly fine some large aggregates. (b) No white material evident.	1.08	1.02	

TABLE XI

Lot No.	Experimental	Stearate		Al. Nitrate soln. (mls.)	Al. Stearate per 100 g. L.S.	Temp. (°C)	Process Remarks	Product (a) Bulk (b) Micro examin.	Bulk Density		Remarks
		Type	Wt.						Butyl Alcohol (g/ml.)	Scoop (g/ml.)	
D.S.15	Stearic acid soln. added to LS + Al.nitrate	Stearic soln.	0.195	1.0	1.0	65	Large aggregates and high proportion of loose crystals in not.	(a) Fine material (b) Some aggregation no white particles evident.	1.19	0.94	Sample sent for test.
D.S.16	Al nitrate soln. diluted to 50 mls.	Solid stearic	"	"	"	"	Small aggregates mainly loose crystals.	(a) Fine material. (b) Very few granules , no white particles.	1.32	1.14	

Appendix VI

Method for the Determination of the Specific Resistance of Initiatory Materials

A method for the routine testing of specific resistance was devised to assess rapidly the electrical leakage of lead styphnate treated with conducting materials. The rapid leakage of electrical charges is necessary to ensure that the electrical energy for ignition is not reached.

The electrification properties of a few products have been investigated and the results are summarised in the various Appendices of this report, but these tests require large quantities of material and can not be used as a rapid routine test to indicate the effect of the various incorporations.

Apparatus

Fig.26 shows the apparatus used for obtaining the resistance of thin layers of treated lead styphnate. It consisted of a brass base with a ¾" diameter recess containing a central spigot (0.595 cms. diameter). An annular method of insulating material with a funnel shaped top, fitted over the spigot. The drift (end diameter 0.595 cms.) was a sliding fit in the mould and could be raised or lowered into the mould through the insulated bearing by the attached string. Attached to the top of the drift was a vernier screw by means of which the thickness of the initiator layer could be measured. The drift and base plate were connected to an instrument for measuring resistance. In practice a Mullard Universal Measuring Bridge (Type GM.4140) was used to give resistances up to 10 x 10^6 ohms; a 500 v. Megger was also used in cases where no readings were obtained with the Mullard Bridge.

Procedure

The apparatus was set up with the mould in position over the spigot, the drift lowered so that it passed freely into the mould and rested on the spigot, in this position the screw vernier was adjusted and the reading noted. The electric leads to the Mullard Bridge were short circuited as a precautionary measure, the drift raised and the material under test which had been measured out by charge plate principle (approx. 0.015 g.) was dropped into the mould. The drift was lowered and tamped with a 215 grm. weight, the leads reconnected to the measuring bridge and the electrical resistance of the layer of material determined. After again short circuiting the leads the vernier was readjusted and the thickness of the layer of initiator determined. The drift was again raised, another increment of material added to the mould and the resistance and thickness of the two increments measured. It was usual to determine the resistance in this manner of at least three increments, then remove the material, clean the spigot, drift, and mould, then repeat the procedure twice.

Some of the materials detonated when using the 500 V Megger and as a safety precaution, the measuring instrument was set up in a different room.

Calculation of Results

The specific resistance is calculated from the formula $\frac{R}{a \times d}$?

$$\text{Sp.Res.} = \frac{R \times a}{d}$$

where R = resistance of the layer measured in ohms; a = area of spigot top (0.268 sq.cms.) and d = thickness of the layer under test (cms.)

Discussion of Method and Results

Various tamping loads and methods for filling the apparatus with the sample under test were tried and it was found that a minimum total tamping load of 400 grms. was necessary in order to consolidate the layer sufficiently to give reproducible values of specific resistance for varying thicknesses of material.

During a larger number of tests it was noted that graphited lead styphnate having a high specific resistance i.e. $< 8,500 \times 10^4$ ohms/cm^3 detonated readily during resistance measurements using the 500 V Megger while untreated lead styphnate would not detonate under these conditions. Graphited lead styphnate containing sufficient graphite to give a specific resistance of the order 50×10^4 ohms/cm^3 gave no detonations with the 500 V Megger.

In Fig.7 the specific resistances have been plotted against the graphite content for three types of lead styphnate which had been graphited by the process using colloidal graphite dispersed in water. It will be seen that for each type of lead styphnate there is a value of the graphite content below which the resistance increases rapidly as the graphite content is decreased, this graphite content is called the "Minimum Graphite Value". Thus in order to obtain a graphited lead styphnate of low specific resistance it is necessary to have a graphite content greater than the minimum value for the particular type of lead styphnate. For the types of material in Fig.7, the minimum graphite value for R.D.1302 (sp. surface area 300-400 cm^2/g) is 1.7% graphite, for R.D.1303 (sp. surface area 700 cm^2/g.) it is 2% graphite and for lead styphnate similar to R.D.1303 but with a specific surface area of 1,000 cm^2/g. it is 2.5% graphite.

The specific resistance of the treated lead styphnate is a good indication of the sensitiveness to static charges of the material in the loose state; products with specific resistances lower than 50×10^4 ohms/cm^3 are practically insensitive to electro static discharges (see electrification tests on CG.19 Appendix I). It is evident from the summary of results below, that, in the loose state, graphited lead styphnate having a graphite content below the minimum value, has a greater static risk than untreated lead styphnate.

Expt.	Type of Material	% graphite	Sp.Res. ohms. $\times 10^4$ /cm.^{3}	Detonation with 500V Megger	Remarks Ref. Appendices
CG.19	Graphited R.D.1303	1.8	43	None	I
CG.19/2	" " "	2.6	2.5	None	I
CG.98) B.II)	" " "	1.42	>10,000	Detonated	II
CG.63	Graphited R.D.1302	1.72	21	None	II
CG.92	" " "	1.18	>10,000	Detonated	II
CG.91	" " "	0.7	>10,000	Detonated	II
S.23	R.D.1302	Nil	>10,000	None	
CG.32	R.D.1303 wet mixed with powdered graphite	9.4	>10,000	Detonated	IV
CG.35	" " " "	12.0	> 19	None	IV

Fig1. CG3 X50 M855.
Graphited R.D.1303. 1% gelatin
3·7% colloidal graphite.

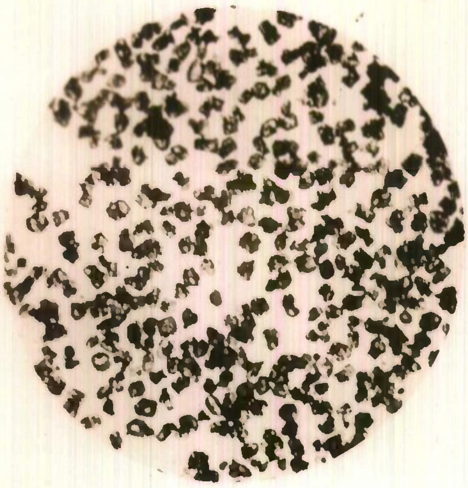


Fig.2. CG19 X50 M825.
120 gm. batch graphited R.D.1303.
0·2% gelatin 1·8% colloidal graphite

Fig.3. CG19 X280 M852.
Enlarged crystals of graphited R.D.1303
showing partial coating.

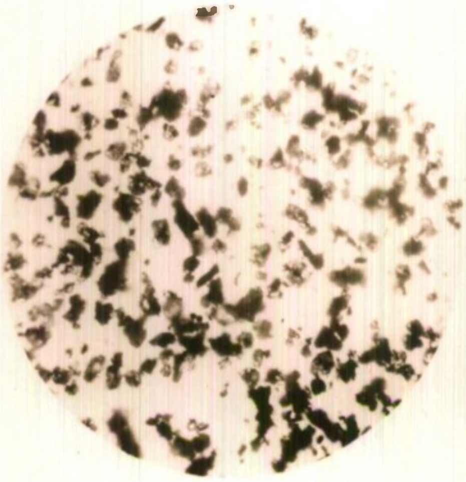


Fig 4. CG19/2 X50 M886
Graphited R.D.1303 mixed with
powdered graphite.

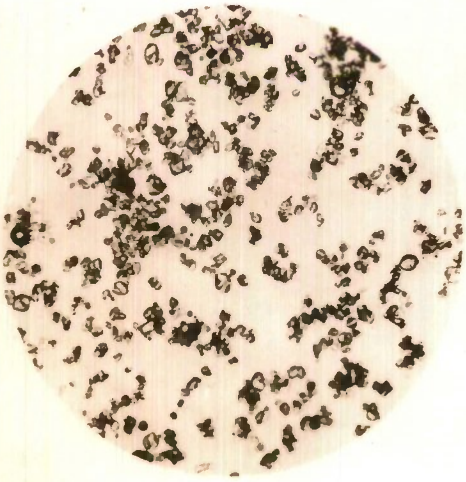


Fig 5. S24 X50 M722.
Untreated R.D.1303

Fig 6. S23 + graphite X50 M846
Mechanical mixture.

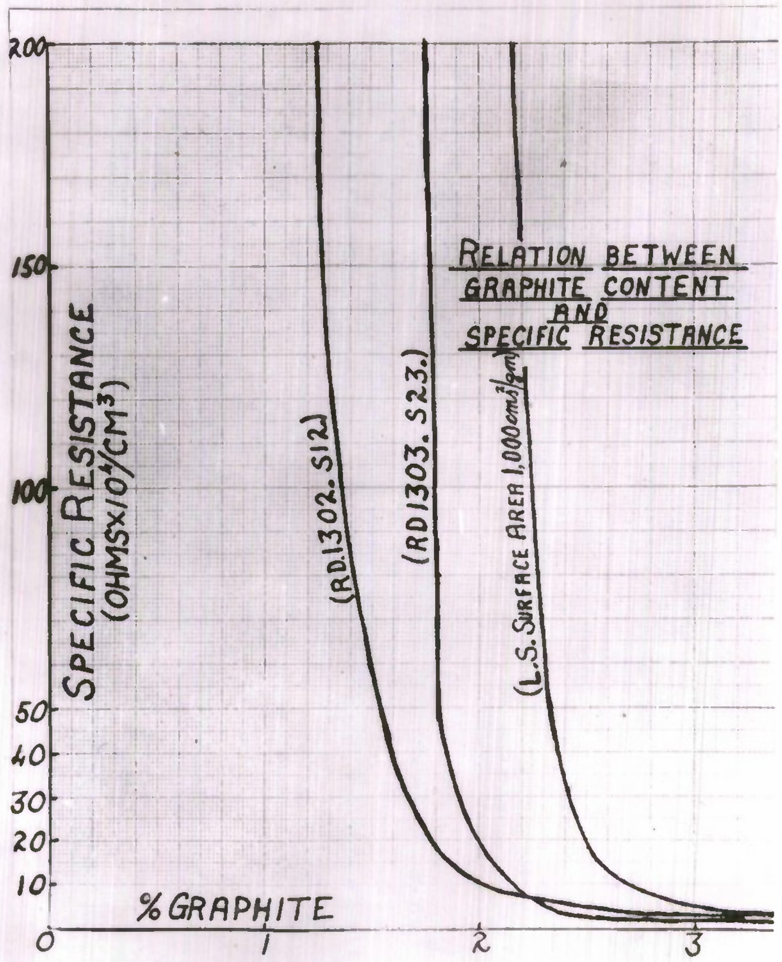


Fig. 7. Relation between graphite content and specific resistence for three types of graphited lead styphnate.

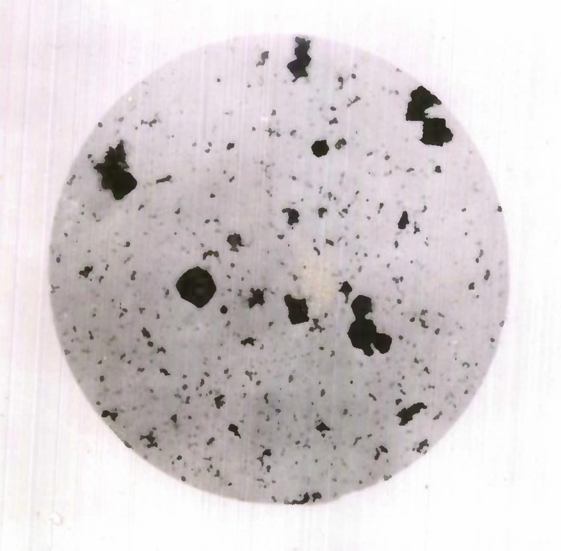


Fig. 8. X50 M 1132
Flocculation of graphite with RD.1303 before addition of gelatin

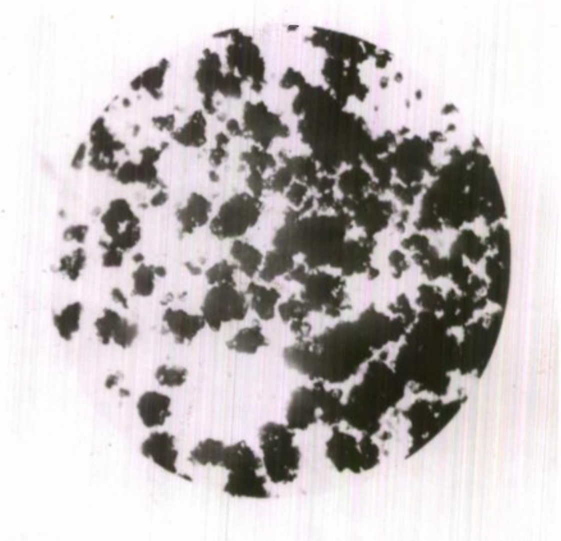


Fig. 9. CG4 X50 M818.
Graphited R.D.1303 containing 6·4% colloidal graphite and 2% gelatin.

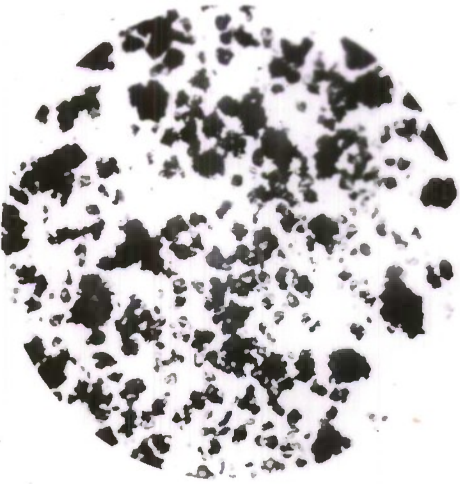


Fig.10. CG8 X50 M819
Graphited R.D.1303 with 4·5% colloidal graphite and 1% gelatin.

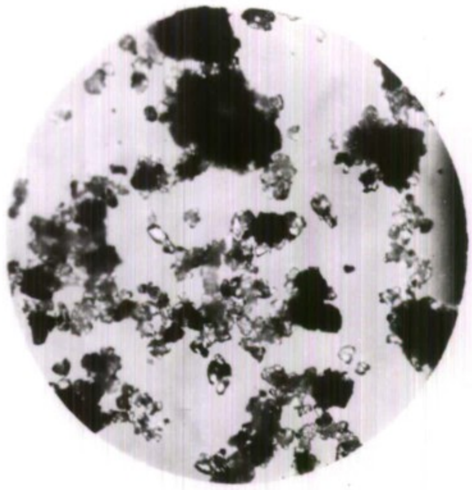


Fig.11. CG11 X50 M854
Graphited R.D.1303 using colloidal graphite dispersed in acetone.
7·6% graphite.

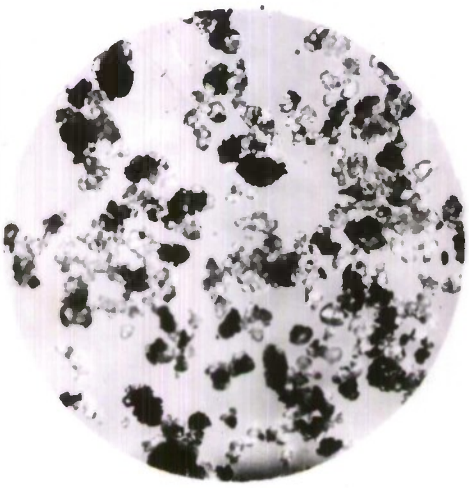


Fig.12. CG13 X50 M857.
Graphited R.D.1303 using colloidal graphite dispersed in CCl_4.
7·65% graphite.

Fig.13. CG15 X50 M858.
Graphited R.D.1303 using colloidal graphite dispersed in CCl_4.
12·6% graphite.

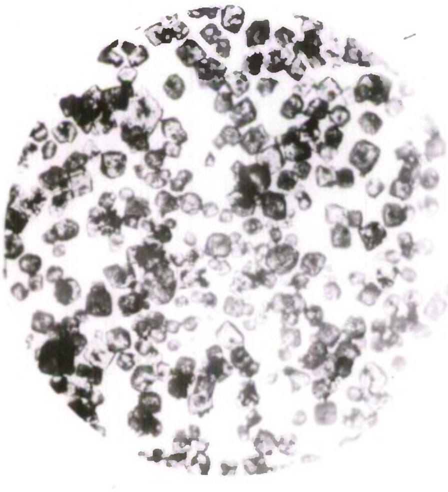


Fig14. CG36. X50 M993
Graphited R.D.1302.

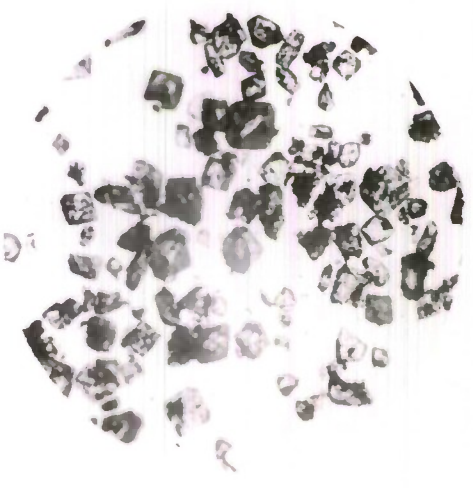


Fig15 CG61 X50 M1008
Graphited Service (I.C.I) lead styphnate

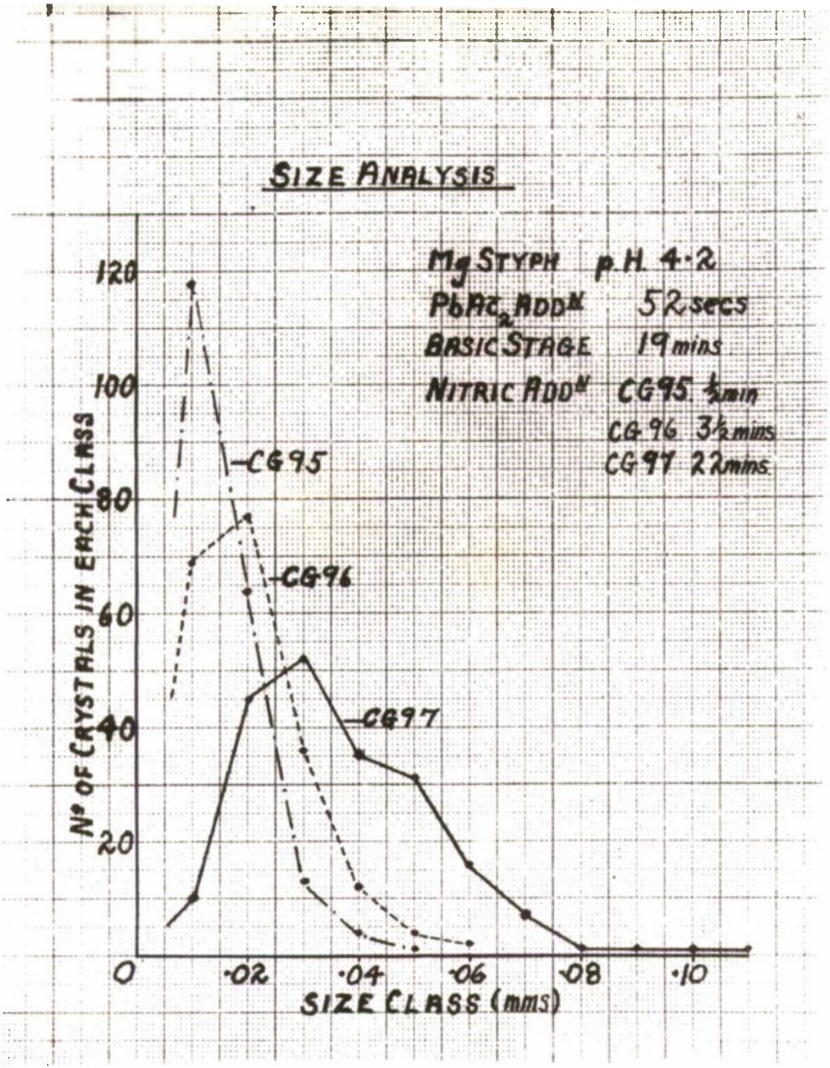


Fig. 16A.

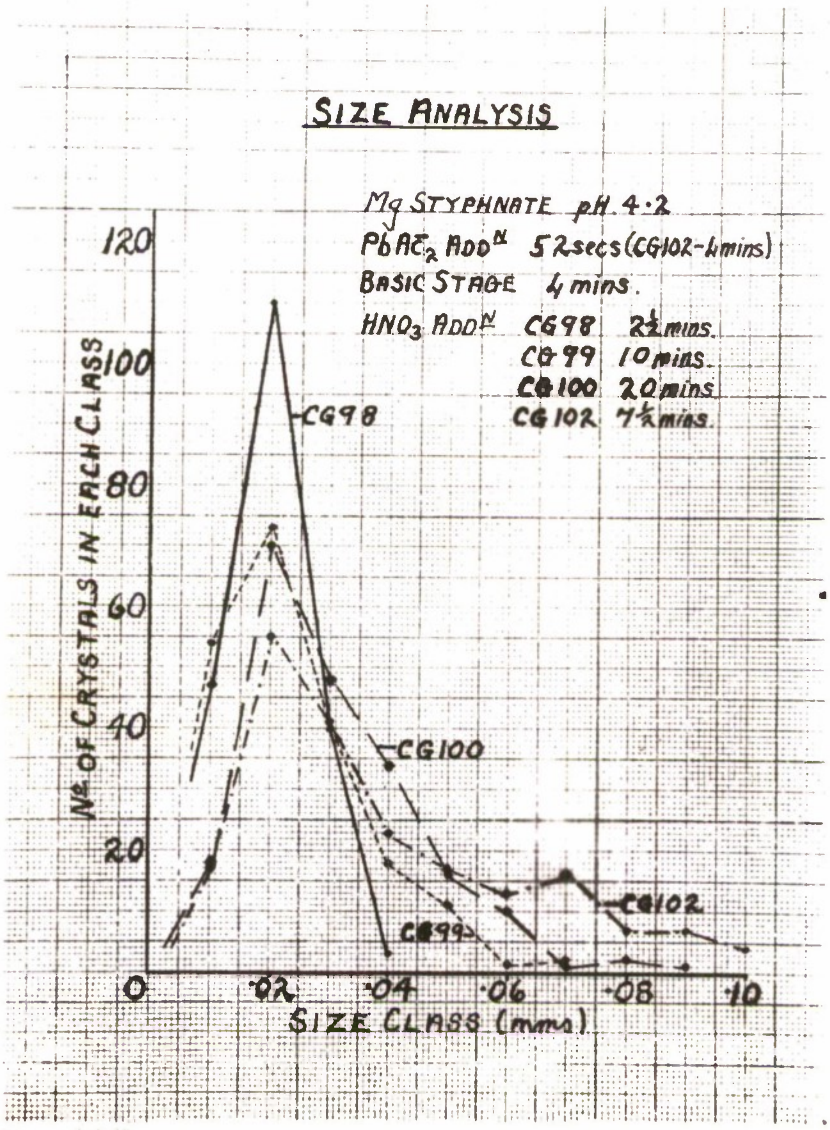


Fig. 16B.

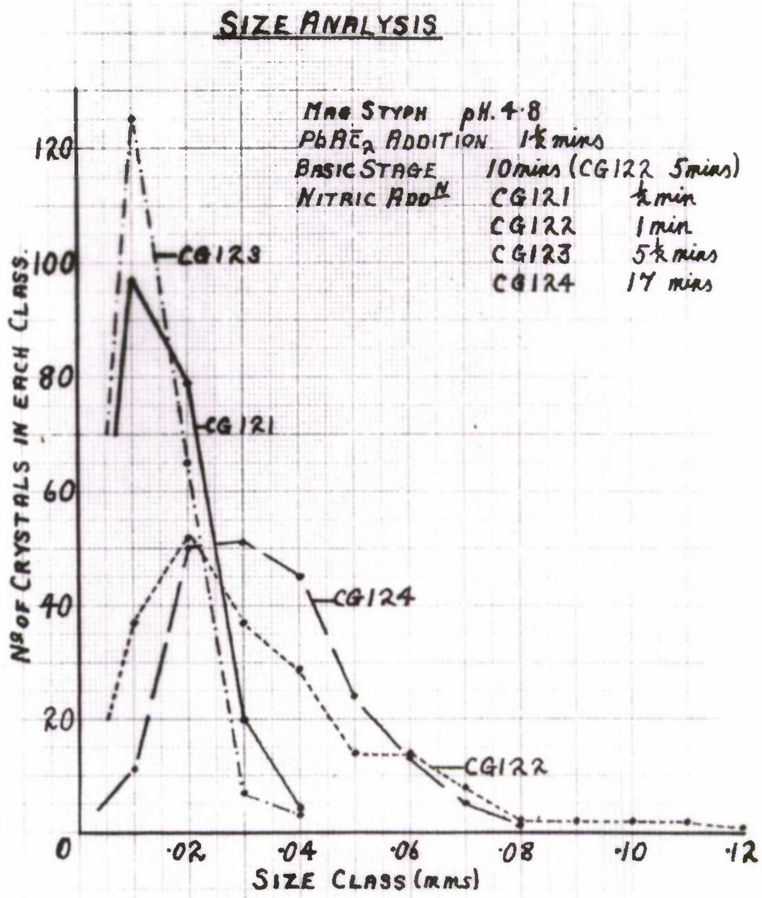


Fig. 16C.

Fig. 17. CG 97 X50 M1045
Tabular type lead styphnate of low specific surface area.

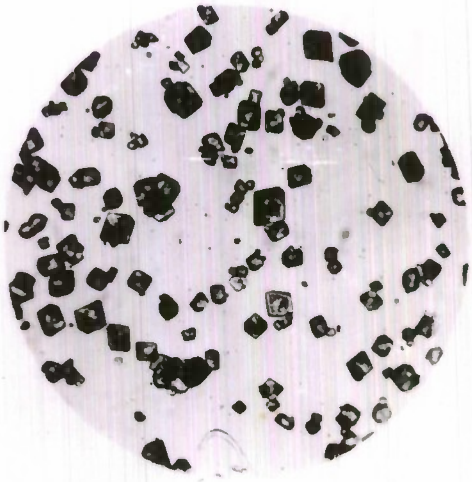


Fig. 18. CG102 X50 M1053.
Equant type of lead styphnate.

Fig.19. CG 34 X50 M889
Wet incorporation of 12·5% powdered graphite.

Fig.20. CG 60 X50 M999
Combination process 130 gm. scale.

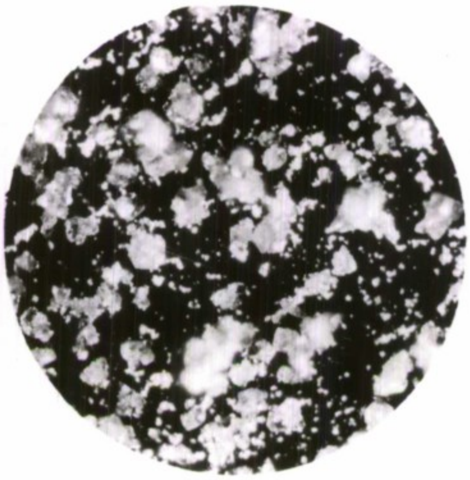


Fig. 21. AS2 X50 M 875
10% incorporation of fine aluminium powder.

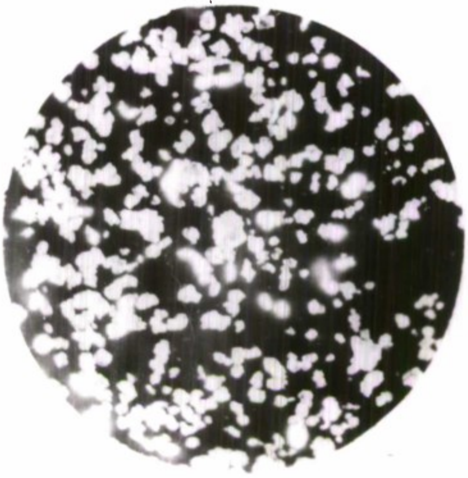


Fig.22. AS 3 X50 M 874
Incorporation of coarse aluminium powder

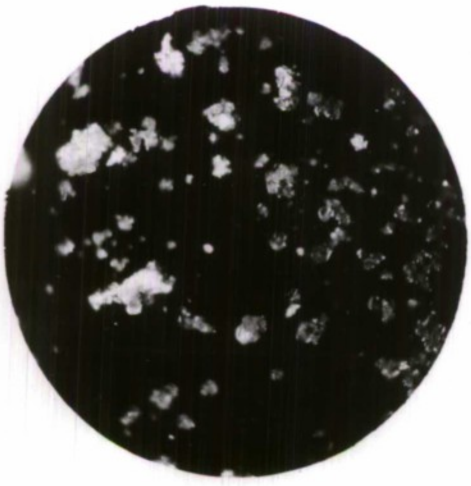


Fig. 23. AS 4 X50 M876
10% incorporation of intermediate size aluminium powder.

Fig. 24. DS 12 X50 M113
Incorporation of 10% aluminium stearate.

Fig. 25. DS8 X50 M1046
Incorporation of 10% aluminium stearate using a solution of stearic acid in alcohol.

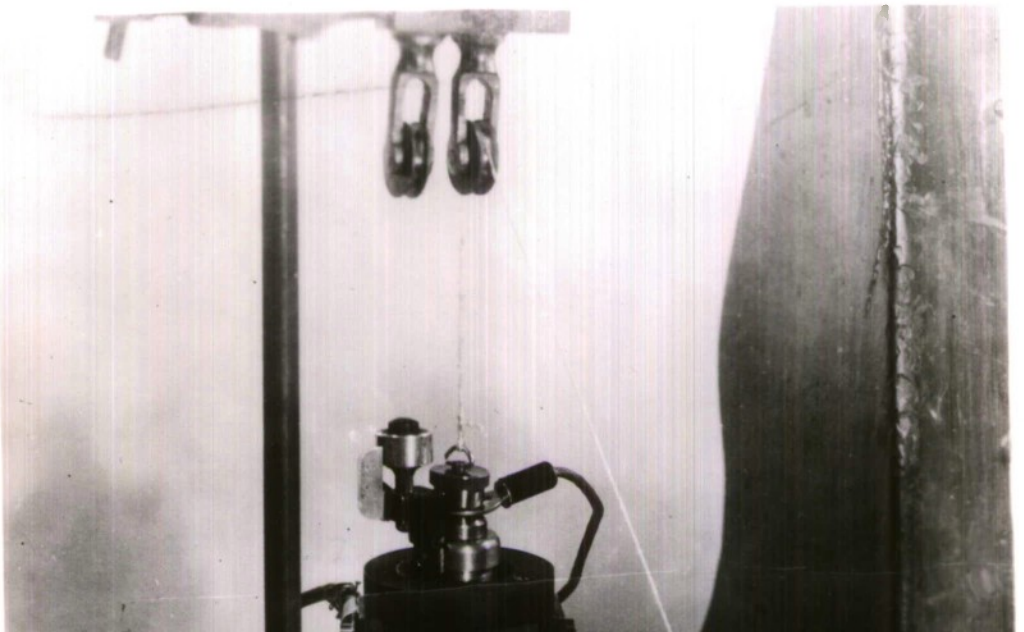


Fig. 26. Apparatus used for specific resistance determinations.