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Summary of Current
Activities of ERDE
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ADVISORY COUNCIL ON SCIENTIFIC RESEARCH
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WEAPONS AND EXPLOSIVES ADVISORY BOARD

A Note on the Current Activities of E.R.D.E.

by D./E.R.D.E.

E.R.D.E. Ref. XR.1370/2.
April, 1957.

Foreword.

This Note follows the pattern set by last year's review, circulated as A.C.13663, and, like that paper, is aimed at helping the Board to visualize the research in progress at E.R.D.E.

As the Chairman of the Board reported to the Scientific Advisory Council on February 20th, the year 1956-57 has not been marked by any startling changes, and the general pattern of work has changed but little. There have, however, been some additions to our programme, and at the same time the new man-power ceiling has prevented us from filling some of the vacancies in our scientific staff; staff deployment has therefore become a more than usually anxious matter. In principle, a situation of this sort calls for no more than a cessation of work on the less important items; in practice, as all experience shows, this is a matter which calls for the most careful consideration.

At the time of writing (March), the main new items concern rubbery composite propellants, based on polyurethane binders, and study of the alkyl boron hydrides, which are under consideration as high-energy fuels for gas turbines and ram jets; the former problem was introduced to the 14th meeting of the Board on 30th May 1956, but the latter was assigned to E.R.D.E. towards the end of 1956. By various shifts, it has been possible to staff these two problems about as fully as is reasonable in the present state of knowledge: if progress is rapid, reinforcement in one or both may be necessary, though it will certainly be hard to provide. Up to now, the men have been made available by suspending work, at appropriate points in time, on some though not necessarily all aspects of the following problems: the carbon monoxide-ammonia-lime cyanamide synthesis, the inhibition of cordite charges, the chemistry of cordite stabilizers, and the chemistry of the impurities encountered in T.N.T. The contemplated programme of work on fluorine, in bi-liquid propellant combinations will also be slowed down. It is almost certain that other suspensions will have to take place, and to this end the prospects of some other investigations

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have been discussed critically and in detail with members of the Committees interested in the work. It cannot be emphasized too strongly that the decision to stop an investigation is never an easy one to take. No investigation is undertaken lightly in the first place, and it is consequently not surprising that the research men themselves and the interested Committee members alike are almost invariably reluctant to assert that no more of value can be secured. Furthermore, on the development side, it is surprising to those who have not experienced it personally to see how much work has to be done after 'development' has been 'completed'; in fact, the commitments in respect of a successful development, such as the E.R.D.E. direct-fusion process for picrite, are often embarrassingly heavy and prolonged. However, at the time of writing, there are grounds for hoping that any further re-deployment, which may be necessary, can be made without drastic disturbance.

On the more positive side, there are some cases where the progress realized calls for special mention. Thus, in the H.E. field, while very little effort indeed has been directed towards seeking completely new types, the H.M.X. work has been carried, if not to a conclusion, at least to the point where a proved process of manufacture exists, and (in collaboration with the users) a satisfactory castable composition devised. In the field of combustion theory, it seems possible that a new 'break-through' has been achieved: this is referred to in more detail below, but it is perhaps worth remarking here that this measure of success was achieved, and could only have been achieved, by the use of a high-speed electronic computer.

In the composite propellant field, the work on the polyurethane compositions has made pleasingly rapid progress in its early stages (though it is far too early to predict its future course); and there has been a rather amusing development with the polyisobutene plastic propellants, which have gone through a process of 'paper upgrading'. These propellants have always performed rather better than was to be expected from the calculated specific impulses; it has now been found that this minor mystery resulted from errors in the accepted heats of formation of ammonium perchlorate and ammonium picrate. Corrected values for both have now appeared in the literature (and, in the latter case, confirmed at E.R.D.E.), and the adoption of these has raised the calculated S.I's of these propellants to figures in good accord with their performance. This is one more illustration of the importance of sound calorimetry in explosive research; and it makes it the more pleasant to report that the E.R.D.E. calorimetric facilities have gradually been built up to a high level.

It is, perhaps, right to end this Foreword by remarking that, as in the previous year, this paper is mainly concerned with items in which "research" or "development" aspects are predominant; little reference is made to the large amount of day-to-day work (by no means all pure routine) which the Establishment has to carry out.

BORON HYDRIDES

As noted above, E.R.D.E. has been instructed to collaborate in the examination of certain alkyl boranes as high-energy fuels. The investigation, which is necessarily extremely complex, is at a very early stage, but it is perhaps worth remarking on the planning of work in its initial stages.

The preferred fuels at the moment are ethyl decaborane and propyl pentaborane (the choice is limited by the need for serviceable physical properties, notably a wide liquid range), and it seems certain that diborane will be the essential intermediate for both. Taking into account this fact, the present intention is that Nanesakuke shall concentrate on the stages leading to diborane, Waltham Abbey shall concentrate on the conversion of diborane to the fuel, and Pyestock on the problems related to the combustion of the fuel.

It is not possible to feel great optimism about the prospects of this work. There are grounds for doubting whether the calculated gain in energy of 40% over hydrocarbon fuels can be fully realized in practice, and the cost of production is not likely to be much less than three orders of magnitude greater than that of kerosine. However, the using authorities consider that there are cases in which

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even a small gain in performance may bring so great a return, in tactical terms, that high costs may prove to be acceptable. In such circumstances, a preliminary investigation in scarcely avoidable; if this turns out promisingly, the scale and complexity of the planning will have to be greatly increased.

COMBUSTION RESEARCH.

(a) Theories of Flame Propagation and their application to Propellant Combustion.

The problem of the propagation of flame in a reactive medium can be formulated in terms of the differential equations of conservation of energy and chemical species. Earlier methods of solution, such as those of Boys and Corner assume a steady, time independent, state and solve the equations for the flow velocity with which the solution satisfies the boundary conditions. These methods, although satisfactory for simple one-step chemical reactions, may fail when applied to complex consecutive or repetitive chain reactions. They are also inapplicable to low pressure solid propellant combustion where experience shows that the propagation is not in a steady, time-independent, state moving in a normal direction to the propellant surface, but occurs in a series of waves propagating laterally in the propellant surface.

Spalding at Imperial College has used a graphical finite difference approximation to the unsteady state equations to solve ignition problems, and has shown that, in principle, the solution may be continued to obtain the steady state flame velocity. This extension, which is too laborious and time consuming when attempted by desk machine computation, becomes practicable with high speed electronic machines.

In collaboration with A.R.D.E. this method has been programmed for the AMOS machine and used to solve the flame propagation equations for a repetitive chain reaction of the Rice-Herzfeld type using the chemical kinetic data suggested for hydrazine decomposition in E.R.D.E. 6/R/52. Calculations have been made of the reactant and temperature distributions for a range of combustion temperatures and pressures together with the resultant steady state flame velocities. The temperature and pressure dependence of the latter are in satisfactory agreement with experimental findings.*

This represents a considerable advance in the application of flame theory in that it is the first instance of the experimental behaviour of a complex decomposition flame having been satisfactorily calculated from chemical kinetic data obtained in classical low temperature kinetic studies. The method, using the existing computer programme, could be applied to other flame problems and is particularly well suited to ignition and flame stability problems.

(b) Platonization Studies.

It has been necessary to slow down the work on the fundamental aspect of platonization, partly owing to the departure of one of the men concerned, but some interesting observations have been recorded by photographing the burning surface of a number of double-base compositions, over a range of pressures. The compositions were chosen to give a selection of burning rates, "mesa" pressures and additives. At low pressure, "hot spots" appear in the photographs which fade out in the region of the "mesa"; and while there is still room for doubt as to the exact significance of this, it can be argued that these "hot spots", which are small particles of amorphous carbon, are centres of catalytic activity responsible for the increased rate of burning at low pressures of a "platonized" composition; their disappearance at the mesa coincides with the fall in burning rate to, or below, that of the unplatonized composition.

An attempt has been made to relate the changes in burning rate produced by a number of metallic oxides with the apparent temperature of the "hot spots" and with the product gas composition close to the burning surface. In general, the increased burning rate is accompanied by an increase in the temperature of the carbon "hot spots", although the effect is not large, and by a reduction in the nitric oxide concentration or an increase in the carbon dioxide concentration in the products. It seems that lead is the most effective metal in increasing the rate of burning because the catalysis is able to commence at a lower temperature than with the other metals, and therefore it has a greater influence on the early stages of the combustion.

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* The experimental data on the hydrazine flame has been thought to be self-conflicting both with regard to the temperature dependence of flame velocity, which is about half that predicted from the activation energy of the decomposition of the hydrazine molecule, and with regard to the pressure dependence which, measured in the vapour below atmospheric pressure, is very small and inconsistent with the supposed first order character of the decomposition. At higher pressures, in the liquid state, the flame velocity is markedly dependent on pressure. The present calculations predict just this behaviour as the result of the chain character of the decomposition in the flame.

INITIATORS

Perhaps the most important development during the year was the arrangement of an extensive series of trials to compare dextrinated lead azide with other types. Such a comparison involves many issues and many interests, and it accordingly seemed desirable to bring the organization of these trials under the aegis of the Ordnance Board, through its Sensitive Azide Working Party. A comprehensive programme, comparing the improved form of dextrinated lead azide (R.D.1352) referred to in the last review, R.D.1343, at present the form of lead azide preferred by E.R.D.E. for general application in detonators, and Service lead azide, has been worked out between D/A.R.D.E., D.O.F./F. and D/E.R.D.E., and all three groups will collaborate in the various aspects of the trials, which will take several months.

Comparisons of this thoroughness do not appear to have been carried out before. Dextrinated lead azide has long been regarded as considerably safer to handle than Service lead azide, but firm conclusions are difficult to draw because the materials have rarely been filled into detonators of identical design, by identical procedures. Oddly enough, the usual impact and friction sensitiveness tests do not distinguish between the materials; the dextrinated material, perhaps because of its hygroscopicity, is distinctly less sensitive to static discharge than the Service material, but static sensitiveness is not the most serious problem with any ordinary form of lead azide. R.D.1352, which is prepared using an anionic dispersing agent as well as dextrin, has been selected for these trials as it has many advantages from the factory point of view: the whole process lends itself to better control and is less critically dependent on the quality of the dextrin (by no means easily specifiable), while the product is of improved physical form and uniformity, and of higher and less variable azide content. It is, however, more hygroscopic than Service lead azide or R.D.1343, and this may be unfavourable to storage life, though its importance will no doubt depend greatly on the design of the detonator and the other ingredients present in the fillings.

More work has been done on the third (gamma) polymorph of lead azide; it has been found that it can be prepared, quite reproducibly, in the presence of polyvinyl alcohol of the 99% hydrolyzed type. On the other hand, many experiments have led to the conclusion that gamma lead azide is unlikely to be encountered in any known processes for making the explosive. Much difficulty has been experienced in preparing samples of the gamma form for technical assessment, but recrystallization from ammonium acetate solution has provided satisfactory specimens for crystallographic study.

Some useful progress has been achieved in the long-standing problem of reducing the electrostatic sensitiveness of lead styphnate.

HIGH EXPLOSIVES

Reference has already been made above to the development of a composition based essentially on H.M.X. and T.N.T. This seems to be satisfactory, and worthwhile in cases where even a small percentage gain is important; but at present H.M.X., although 'accessible', is still obtained in poorer yields than R.D.X., and accordingly the emphasis in this field has been shifted to a detailed study of the reactions involved in its production. This is a complicated affair, because the numbers of initial reactants, and, still more, of the reacting molecular species, are unusually large, but a step-by-step approach is bringing up useful information.

/It

It has been possible to start work on the new process for the preparation of T.N.T., and the apparatus is almost complete. This is designed to produce some 4 lbs. of T.N.T. per hour, in a continuous process starting from toluene. (The existing R.O.F. procedure starts from mononitrotoluene). The new process has been under discussion with the T.N.T. Working Party, members of which have expressed a good deal of interest in the unit being set up. It is expected that it will turn out considerably more T.N.T., in relation to its size, than the older plants, and it is hoped that the product will be of better quality. However, to get full value from it, oleum will be needed, and this aspect (which falls within the sphere of the R.O.F. organization) will require study.

The investigation of the pick-up sensitivity of R.D.X., referred to briefly in the last review, has grown into one of E.R.D.E's major pre-occupations. The points at issue are rather subtle, and new methods of investigation have had to be devised both for the detonation tests, and for the laboratory investigations; these are referred to in the next section. It appears that real differences in sensitivity do occur, and that these seem to be associated with the number and type of voids in the crystals; it is possible also that the inclusions in these voids are of importance. Results to date indicate that high pick-up sensitivity is associated with a large number of voids in the crystals, and that the presence of these can be ensured by partial recrystallization of Bachman, but not of nitrolysis, process R.D.X. However, it is not easy to secure these characteristics and, at the same time, good pourability of the R.D.X./T.N.T. mixture made from the crystallized material.

The rate of crystallization of R.D.X. from nitric acid solution is also under study in a separate investigation, related to the nitrolysis process operated in the R.O.F's. The results are likely to have a considerable influence on previously-contemplated developments; it seems, for example, that an Oslo-type crystallizer, which was under consideration, would have to be impracticably large, and other proposals are now being examined.

PICK-UP SENSITIVITY

In ordnance assemblies the sequence: explosive/metal/explosive commonly occurs. This system can be used to test the sensitivity of the second explosive in terms of the thickness of the metal barrier required to prevent its explosion. The 'sensitivity' so measured is of importance in considering explosives in relation to weapon functioning, but is not necessarily indicative of the relative hazard in handling the explosive concerned.

A detailed study is being made of the operation of such a test (which is a version of the well-known 'gap' test). It has been found that a shock wave is sent into the second explosive and this shock may either decelerate and fade or accelerate into a detonation. This process develops in a smooth and continuous manner (but not at a uniform rate) and it is presumed that energy is liberated in the train of the shock and it is the balance of energy loss to energy released that decides the fate of the test. A most important observation is that the sensitivity as measured is the average of the sensitiveness of the components weighted according to the proportion present. Thus it has been found possible to add small proportions of materials of extreme sensitivity with a negligible effect on the result (e.g. 1% of an H.M.X. with an impact sensitiveness of the same order as mercury fulminate has been added to a 60/40 R.D.X./T.N.T.) This is in agreement with the foregoing hypothesis since although the sensitive material, by reason of its sensitivity, will react quickly to the shock, the total amount of energy it can provide is very small. Small holes (bubbles) and other sensitizing nuclei may be considered to contribute (but not necessarily control) in the same way whether they operate by providing 'hot spots' on adiabatic compression or by providing surface for hetrogenous reactions. A number of samples of 60/40 R.D.X./T.N.T. have been examined by this method and it has been found that the sensitivity is almost entirely controlled by the R.D.X. and moreover the R.D.X's which yield the most sensitive R.D.X./T.N.T's all contain numerous inclusions. If these inclusions are removed by a suitable

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crystallization procedure, the sensitivity of the product R.D.X./T.N.T. drops, and if the number of inclusions is increased the sensitivity rises. While it is possible that small quantities of impurities play a part, it is thought that the most important factor is the internal surfaces of these voids in the R.D.X. crystal which are, of course, not coated with the T.N.T.

HIGH VELOCITY PROJECTILE ATTACK

Apparatus has been set up to study the factors controlling the probability of explosion of H.E. under projectile attack. The standard projectile is an annealed steel sphere weighing 8.3 grams and the maximum velocity is in the region of 2500 metres per second. It is proposed to compare the probability of explosion and the mechanism by which this occurs with that initiated by an explosive/metal ('gap') system. An insufficient number of explosives have been examined to form firm conclusions based on a comparison of the probabilities of explosion, but there is evidence of a marked similarity in the sequence of events following either from initiation, viz. that a shock is sent into the charge under test and this builds up into a detonation. It may be assumed from this that the most important factor controlling the sensitivity is the rate of reaction, and therefore energy release, at pressures found in shock waves travelling at about 3000 m.p.s. in the explosive. If this is so, then the probability of explosion will not be controlled by the probability of initiation, but by the rate at which energy is released in shock waves of moderate intensity, and the most sensitive material will be the one in which energy is released fastest at these (relatively) low pressures. As with the 'gap' test holes, flaws and other sensitizing nuclei will only contribute a quota to the speed of the process and not necessarily dominate it.

COMPOSITE PROPELLANTS FOR ROCKETS

As has been noted above, particular attention is being given to the development of castable composite propellants using polyurethane binders. Although this stems directly from U.S. work, it does not take the form of an exact duplication of any American development, and in several ways we shall be studying aspects or developments which, we believe, have not been fully covered in American or earlier work.

The E.R.D.E. investigation is being carried out at present in two distinct parts, one concerned with studying the compounding operations, and the other devoted to extending basic knowledge of the relations between chemical structure and physical properties in the polymer.

The former investigation has been made possible, at this early stage, by the fortunate circumstance that there is a commercial material, produced in this country, but differing from the materials so far used by most of the American groups, the properties of which appear to approximate fairly closely to our needs. The existence of this material has made it possible to investigate the finer details of processing, which, it is well known, are decisive with this class of material; our conditions, in which we finish with a composition containing 70 to 80% of solids, naturally differ greatly from the commercial usage of the material. There are many difficulties to be overcome, but at present they do not appear to be insuperable.

In the other investigation, a wide range of polyurethane rubbers are being made, and tested for physical properties, in the first place in the unloaded state. Among these tests, one of particular importance is that determining the brittle point, for which purpose the B.S. test, based on the Clash and Berg procedure, is being used. It is often argued that the second-order transition point represents a more 'fundamental' measure than the brittle point, but E.R.D.E. experience is that the Clash and Berg test gives a direct and unambiguous, if empirical, measure of what is required in practice, while the determination of the second-order transition point is in fact a much more involved business than might be supposed.

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Very few firings have been carried out so far, though what has been done has been encouraging. It is hoped to fill a few 5 in. motors before long, but it is exceedingly important to realize that, however well the preliminary trials may go, a prolonged period of testing (not least as regards storage tests) must take place before one can attempt to forecast the future of this project.

At the present time, work on the older plastic propellants, of the ammonium perchlorate-ammonium picrate-polyisobutene type, has passed over almost entirely to the development level, entailing almost continuous collaboration with R.O.F. Bridgwater on the one hand and R.A.E. Westcott on the other. However, during the year, an important advance was made in respect of what may be called a 'plasticized binder' for this class of propellant.

Low temperature firings, at -30°F and below, of the 2-inch aircraft rocket filled P.I.B. type plastic propellant, had shown that the physical properties of the propellant are marginal in this particular case. A modified composition has now been developed, based on polyisobutene plasticized with ethyl oleate as the binder, in conjunction with synthetic surface active agents in place of lecithin. Laboratory tests have shown that the new propellant is much superior to the normal P.I.B./lecithin type at low temperatures, although it is still marginal in the 2-inch aircraft rocket at -40°F. The number of bursts, at -30°F or below, has now been reduced to about 1 in 600, which makes the assessment of possible further improvements very difficult. Alternative ignition systems currently being studied may be one way of reducing the incidence of bursts.

The new propellant has a definite retarded elastic component at low temperatures, and this has led to a very useful laboratory test for the measurement of elastic deformability, which helps to distinguish between various plastic propellants at low temperatures. The strain rates used are typical of those involved in the pressurisation of a rocket on ignition.

Another new development has been two 'platonized' compositions, achieved by the use of bimodal oxidizer size distribution plus a modified processing technique.

In all these studies, rheological considerations are naturally of the utmost importance, but unfortunately, the appropriate branch of rheology, that dealing with stiff pastes, has been little studied outside E.R.D.E.

For many years, flow properties of plastic propellants have been measured with a concentric cylinder plastometer which enables the stress-strain-time relation to be determined in absolute terms. The results are obtained as a series of flow (D/τ) curves, each relating to a particular state of strain. It has been usual to idealise the curves into a series of parallel straight lines corresponding to the equation:

$$D = \frac{dy}{dt} = \frac{\tau - (Y + ay)}{\eta_p} \qquad (1)$$

where y is the shear strain, τ the shearing stress, Y the yield value of the unstrained material, 'a' a coefficient of strain hardening and η_p the plasto-viscosity. The flow properties can therefore be characterised by three parameters, η_p, Y and a.

During the last year, attempts have been made to determine size limitations of plastic propellant rocket charges with regard to resistance to gravitation and set-back by the application of equation (1) and the measured values of the flow parameters. The supporting effect of end rings is a complication and photo-elastic studies have been made to determine the importance of this factor.

Attempts have also been made to improve the flow equation and a better fit with experimental results is given by:

$$\frac{dy}{dt} = \frac{\tau - Y}{\eta_p} \exp.(-\alpha y) \qquad (2)$$

where η_p and Y have the same numerical values as in (1) and α, a dimensionless strain hardening factor, replaces 'a', a strain hardening factor having the dimensions of stress.

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Owing to the time-consuming nature of the absolute flow determinations, attempts have been made to correlate the results with those of simple compression experiments. By making arbitrary assumptions regarding the nature of the shear stresses and strains involved in compression, fairly good correlation can be obtained by applying equation (2). An E.R.D.E. report on this work will shortly be published.

A particular case, in which the rheological problems concerned have aroused lively controversy, concerns the 2.75" gun-assisted rocket. It has been suggested that a rubbery propellant would be essential for this weapon, but E.R.D.E. opinion is not convinced on this point, for approximate calculations suggest that plastic propellants of the current type should perform adequately.

A plastic propellant with a suitable burning rate for this project has accordingly been developed. This is E.3176 which burns at 1.04 inch/sec. at 1000 psi; the pressure exponent is 0.62.

Seven motors have been filled with an inert propellant in the suggested cone and cylinder charge and these have been temperature cycled between -40°F and +140°F twenty times (1 day at each temperature extreme for each cycle) without any sign of failure. Another seventeen motors filled with inert propellant will be projected at Shoeburyness to determine the distortion of the charge when subjected to longitudinal and spin acceleration in the gun.

Attempts are also being made to obtain a theoretical solution to the problem of distortion under the high accelerations involved, and Professor Oldroyd has agreed to help with this work.

COLLOIDAL PROPELLANTS

Work in the colloidal propellant field has been seriously handicapped by the prolonged delay in the completion of Project III, a combined facility designed to bring together the excessively scattered work in this field. When this facility is complete, it will undoubtedly provide a complex of experimental and pilot plants of exceptional value, both by reason of its completeness and by reason of its compactness, the latter point being especially valuable because it enables the supervisory staff to be used much more economically.

Work has continued on ballpowder during the year, and a good deal of progress has been made. The knowledge so acquired is likely to prove highly advantageous when the new commercially-designed unit starts operations at R.O.F. Bishopton.

Meanwhile, great efforts are being put into the study of the small but apparently consistent and statistically-significant differences in the quality of Cordite PU produced by R.O.F. Bishopton, and R.N.P.F. Caerwent. The problem is singularly subtle, and a most searching investigation, over many issues, has become necessary. The staff of the two factories, of the two Inspection Services, and of E.R.D.E., are collaborating very closely in this work.

As regards gun propellants, work during the year has not been on an extensive scale, but a good deal has had to be done in connexion with the 40 m.m. L.70 gun.

The N.A.T.O. countries favour a moderated single base powder for use in the 40 m.m. L.70 gun. There is no experience of this type of propellant in this country and it was decided to develop a ballistic solution on the basis of N/M. The first gun erosion trial with N/M 024 processed at E.R.D.E. has given promising results and manufacture of a few production batches is proceeding at R.O.F. Bishopton. Some difficulties are being experienced in controlling vivacity to the required degree but it is thought that adequate control will be achieved by means of Closed Vessel firings.

Parallel work is also proceeding to develop a single base powder but ballistic regularity has not been satisfactory; the irregularity may be associated with the hygroscopicity of this type of powder. Further manufacturing trials are in hand.

/Picrite

PICRITE

It is often supposed that, programme-wise, picrite is dead. In practice, it has taken a great deal of effort during the past year, and our commitments are still by no means finished.

The main load has, of course, come from our 'post-development' commitments on the Direct Fusion process, which may be described as having achieved international recognition. A plant of this type is nearing completion at Bishopton, and another is about to be erected in France, while a third one, of very large size, is being set up in the U.S. It seems likely that collaboration with D.O.F./X. in bringing the Bishopton plant into operation would require a fairly substantial effort from E.R.D.E. in the coming months, and a certain amount of time is likely to be taken up with discussions and visits on the French unit. Collaboration with the Americans has taken an even more active form; both in 1955 and 1956, U.S. teams worked with E.R.D.E. personnel on the E.R.D.E. plant, each time for a period of several weeks, in order to examine in detail the direct fusion process itself and the subsequent nitration state.

There are, however, several other picrite processes to be considered from the research point of view; indeed, one imagines that few explosive ingredients can be made by so many different routes. The list includes the Roberts iso-urea process, the ammonium thiocyanate process; the ammonium sulphamate process; the very interesting route, recently discovered in the U.S., in which urea and ammonium nitrate are reacted together in the presence of silica gel; while it is also necessary to note the Chard process for making cyanamide from ammonia, carbon monoxide and lime, which, fitted to the direct fusion process, would remove the present dependence of the latter on calcium carbide.

Of these the Roberts iso-urea process has been operated at the Naval Powder Factory, Indian Head, Md., but the difficulties of ensuring supplies of diethyl sulphate at an attractive price have prevented the further exploitation of the process. The ammonium sulphamate process, examined in Canada, appears to have been dropped, and the rather unfavourable economics of sulphur recovery in the thiocyanate process have discouraged interest in it in the U.K., although it has received a good deal of study in the U.S. and Canada in the past two years. The current E.R.D.E. view, however, is that the urea-ammonium nitrate-silica gel process offers greater potentialities than any of its competitors.

This process was brought to light in a U.S. industrial laboratory, and has been studied at E.R.D.E., with the encouragement of the American authorities, over the past year. The results have been most encouraging; a small glass apparatus has been set up which works a continuous version of the process, and has been operating for some months, and an ingenious new guanidine nitrate crystallization step has been devised which should increase the inherent economic advantages of the process.

It is not easy to decide how far to take this work. As one would expect, many problems of a chemical engineering type would have to be solved before the process could be put on a plant basis, but it seems questionable whether this work should be undertaken, since the demand for picrite has diminished greatly. It is hoped to be possible to produce a report on the laboratory studies by the summer; it will be time enough to consider policy when this report is available.

Laboratory work on the Chard cyanamide process is being brought to a close. This process differs in principle from those mentioned above, since it provides an alternative route to the starting-material of the direct fusion process, but it seems that the present laboratory investigation has reached the stage of diminishing returns. The situation, however, is in reality reasonably satisfactory; the laboratory and pilot plant studies carried out in the preceding years have resulted in the development of a process which is agreed to be usable, even if there is still room for improvement.

/Nitrocellulose

NITROCELLULOSE STUDIES

An extensive series of trials of wood pulp blends, from North American sources, which has involved the collaboration of a paper mill, R.N.P.F. (Caerwent) and E.R.D.E., is drawing to a close. It is not easy to provide a succinct summary of the findings, but it can be said that while some difficulties were encountered in the first series of trials, and it was necessary to make adjustments to the degree of refining of the pulps and to the basis weights of these papers, at least one of the blends performed very well. Blends of 50% bleached sulphate and 50% sulphite pulp were used in each case. Cordite charges produced in the earlier series of trials are undergoing storage trials.

Some investigations of a more academic nature have been in progress for a considerable time, aiming at throwing new light on the chemistry of the stabilization of N.C. by boiling, a matter of particular interest in view of the very long treatments conventionally given to N.C. made by mechanical nitration. Particular attention has been given to the nature of the 'acidity' developed by certain grades of N.C. in acetone solution, and to the nature and amount of oxidized groups in N.C. Interesting results have been obtained, but further advance has been hindered by the very great difficulty of devising analytical methods which will work with the necessary high precision and high sensitivity in this very complex system.

Investigations are also proceeding on the thermal decomposition of N.C. This work, which was originally planned to throw light on the mechanism of platonization, has also encountered serious experimental difficulties, but there seems to be a fair chance that these are being overcome. In this work, N.C. is heated in solution, in the presence or absence of lead compounds, and the gases evolved are measured and analyzed. Much difficulty has been experienced in selecting a solvent which is sufficiently non-reactive in the conditions used, but it seems that m dinitrobenzene may prove adequate. It appears that the addition of litharge does not greatly affect the apparent first-order rate constant of the decomposition, or the induction period, but it does markedly affect the composition of the gaseous products in the later stages of decomposition.

ANALYTICAL INVESTIGATIONS

(a) Thermal Decomposition of Lead Compounds

The thermal decomposition of lead salts of organic acids has been studied by the methods of differential thermal analysis (D.T.A.) and thermogravimetry. D.T.A. records the nature and extent of the endo- or exo-thermal reactions which occur during decomposition, whilst thermogravimetry follows the changes of weight, with temperature. The two techniques together have led to some interesting results. For example on heating in air lead oxalate decomposes directly at 320°C to lead oxide, whereas lead salicylate decomposes in two distinct phases, passing through the basic salt. In air, these reactions are all exothermal indicating that reaction with oxygen is involved. Parallel experiments in nitrogen show an endothermal reaction as expected with a non-stoichiometric product including lead oxide, metallic lead and carbon. To simulate to some extent the conditions occurring during burning of propellants some preliminary studies have also been made in NO_2. All the lead compounds studied so far nitrate rapidly and the products break down on further heating, sometimes with some violence and often at much lower temperatures than the parent product heated in air. It is hoped that studies along these lines may lead to some understanding of the nature of the reactions which occur in platonized propellants.

(b) The Stability of Propellants and the Taliani Test.

The Taliani test as at present used in the U.S. is a measure of the pressure changes which occur on heating a propellant under a constant volume of nitrogen or oxygen. The two gases give different results and the latter is claimed to have the greater significance as an initial fall in pressure occurs followed later by a substantial rise. The period before the rise occurs is claimed to be a measure of the propellant stability. This test is of considerable importance as it

/offers

offers a possible method by which the relative stabilities of propellants can be assessed in a few hours instead of many weeks, and is therefore being studied in some detail. Preliminary studies show that the interpretation of the results suggested by the U.S. workers is over-simplified as even when an excess of oxygen is always present the shape of the Taliani curve is dependent upon the oxygen/propellant ratio. Further, the times to 100 m.m. pressure increase as expected as the stabiliser content is increased by stages from one to three per cent, but thereafter they decline so that propellants with 9 per cent stabiliser fall between the 1 and 2 per cent values. This may be linked to the fact that nitration reactions are favoured at low stabiliser concentrations and nitrosation reactions at high ones. It is hoped that this work will lead to a better understanding of the reactions which occur in this test and analytical studies are being carried out on the gaseous and solid end products with this in view.

(c) Vapour Phase Chromatography.

The technique of vapour phase chromatography has now passed beyond the exploratory stage and the following determinations are now made on a rapid routine basis as required. Estimations of alcohol, acetone, ethyl acetate, methyl methacrylate and water in different types of propellants are now practicable and the method is being used also for such purposes as the estimation of secondary butanol in ethyl nitrate and for the detection and identification of other impurities. The nature of the gases produced during the decomposition of propellants is also under investigation. A small preparative column has recently been constructed capable of taking loads of up to half a gram. This should allow the separation of complex mixtures into individual components in sufficient amounts for spectroscopic study.

ULTRASONIC FLAW DETECTOR

Considerable progress has been recorded with the E.R.D.E. Ultrasonic Flaw Detector. A more compact model, designed and built at E.R.D.E. as a production prototype, was exhibited at the 1956 Exhibition of the Physical Society, and attracted attention from visitors and correspondents from several countries, and from a wide range of specialist interest - from pen manufacturers to paediatricians in fact. Since then, some commercially-produced copies of this equipment have been delivered, and some more will arrive shortly; these equipments will be installed in various explosive factories and research establishments.

Work is now proceeding on the development of test-routines for certain fairly large charges. (The initial requirement was for the examination of the 3-in. cruciform charge, but this is becoming less important). In the course of this work, it has become clear that certain charge designs have cross-sections which are not only difficult to extrude, but also to inspect, by any method. It seems clear that, in the future, the charge designer will have to take into account both the difficulties faced by the manufacturer and those faced by the inspection authorities.

H.T.P.

For the last two years, E.R.D.E. has been heavily engaged in the work on H.T.P. The Establishment is not directly concerned either with the manufacture or the use of the material, but makes its contribution in respect of the extremely difficult problems concerned with its specification and testing, and with its stability and sensitiveness. The work, which is co-ordinated with other interested groups by a Working Party under D.M.X.R.D., is divided as follows:-

(i) The development of techniques necessary to study the changes which occur in H.T.P. on storage and the mechanism of decomposition of hydrogen peroxide.

(ii) The rationale of the stabilization of H.T.P. with sodium stannate.

(iii) Investigations concerned with the specifications of H.T.P. made both by the electrolytic and by the organic processes.

/Experimentally

Experimentally, the work is made most difficult by reason of the susceptibility of hydrogen peroxide to catalytic decomposition provoked by minute traces of adventitious impurities, with the result that it is always hard to secure reproducible results even in seemingly rigorously controlled experiments. The instrumental difficulties in devising a reliable and satisfactory means of measuring the rate of oxygen evolution have also been great, and until recently most methods were liable to be upset by the fact that, initially, the H.T.P. is supersaturated with oxygen, and the capricious release of this oxygen disturbed any gasometric method. Recently, however, the Hersh cell has been brought into use, and this very ingenious device may enable even very low rates of oxygen release to be recorded automatically.

Working hypotheses regarding the function of sodium stannate have been developed, and these are being used in the planning of the experimental work, but are not sufficiently firmly established to be recorded here. An interesting side-issue has been the spectographic confirmation that sodium stannate has the structure $Sn(OMe)_6$.

The E.R.D.E. research is organized in close collaboration with Professor Wynne-Jones's extra-mural group, in which some important advances have been made, notably as regards the establishment of a "pH" scale in concentrated hydrogen peroxide (a matter of fundamental importance) and as regards the mechanism of the catalysis of decomposition by iron and copper.

In addition to these investigations, which are essentially of the 'research' type, a very considerable effort has had to be directed towards the establishment of analytical procedures suitable for specification purposes. A particularly difficult issue has concerned the determination of carbon in H.T.P. made by non-electrolytic processes; the matter is particularly important because of its relation to the shock-sensitiveness of the material, and awkward because it is hard to secure the necessary precision at the very small concentration concerned. The recognized methods were developed to work at concentrations around 300 parts per million, but it is now desired to work below 80 parts per million. Some progress has been achieved.

ORGANIZATIONAL MATTERS

(a) Staff

In the last review, attention was called to the difficulties being caused by the rapid turn-over in staff, especially in the Scientific Officer grades. That review was, however, necessarily presented before the present drive for economy came into effect, with its man-power ceilings. These ceilings, being concerned primarily with the totals of non-industrial staff, and not so much with the numbers in the individual non-industrial grades, work in a complicated way, and all that can be said here is that, within the new limits, E.R.D.E. has very few vacancies on the non-industrial side. On the industrial side, recruitment improved markedly for a time in 1956, but this improvement did not last, and the situation remains difficult.

(b) Facilities

It is sad to have to report that the delays in getting Project III, the integrated colloidal propellant facility, have been considerably greater than was expected, and only isolated parts are in operation now; much equipment, purchased as part of the Project, and not in the usual manner, has turned out to need rectification of one kind or another, and arranging this has given rise to much difficulty. However, progress has been made, and most of the Project should be available for use by the early summer; and when that stage is reached, E.R.D.E. will have a colloidal propellant facility which, in its wideness of scope and adaptability, is probably not matched elsewhere.

/The

The chemical engineering project - perhaps better described in terms of process research - referred to as Project IV - has unfortunately become one of the casualties of the economy drive. It is hoped, however, to save some of the objectives of the plan, and a scheme devised to provide some of the most-urgently needed facilities, at a relatively modest cost, is under study.

Meanwhile, a scheme to recondition some of the still-unconverted R.G.P.F. buildings on North Site as laboratories has been authorized, and a contractor is at work. This will provide new laboratories for the S.E.I. group (essentially organic chemistry), the Analytical Services and a so-called Ballistic Assessment laboratory. The need for all of these is acute, not least because the new arrangements, by bringing the various sub-sections closer together, will enable the time of the supervisory staff to be used more efficiently - an exceedingly important matter, especially in view of the numerous staff changes which have occurred.

It is pleasant to be able to report that, in general, the E.R.D.E. laboratories continue to be well equipped by any standard; the buying policy which has been maintained for many years has provided the Establishment with the wide range of high grade equipment which is absolutely indispensable in view of its position as a sort of court of appeal in explosives chemistry. Two most welcome recent additions, both of American origin, are a Micromerograph, generally regarded as the reference-standard instrument for particle size determination, and a Beckman and Whitley ultra-rapid framing camera. Only the latter has been installed at the time of writing, but it has already provided some most valuable information; incidentally, the image-quality is surprisingly good, and a set of 'unclassified' pictures taken with this instrument will be exhibited at a photographic exhibition in the summer.

(c) Scientific Problems for Discussion with the Board or its Committees.

In the last review, nine topics were listed which, it was thought, would profit by discussion during visits to the Establishment of members of Committees; and it is pleasant to report that a number of such visits have been paid. It was expected that there would be a certain amount of formality about the planning and recording of these visits, but the writer is coming to the view that any great insistence on the strict definition of 'topics' is a serious mistake.

The list of topics, given last year, was carefully drawn up to indicate certain continuing lines of interest, not too narrowly defined, and it consequently holds good today, for the most part; but experience shows that it is not very practicable, or even desirable, to hold our visitors very strictly to this list. Our current practice is to arrange an ad hoc programme for each visit, this programme taking in the topics on the list but not necessarily dominated by them; afterwards, a brief record of the visit is drawn up and circulated to the appropriate Committee. This procedure, while flexible and informal, seems to work smoothly, and to keep the Committees concerned reasonably aware of the outcome of the discussions.

Subject to these considerations, the amended list of topics is as follows:-

(i) T.N.T. Production.
(ii) Crystallization studies.
(iii) Drying of explosives.
(iv) Combustion processes in double base propellants.
(v) Combustion processes in composite propellants.
(vi) Surface chemistry of solid oxidants etc. in relation to propellant binders.
(vii) The passage from initiation to detonation.