The dish is gently heated over a low flame so that the liquid fumes moderately for three minutes. If a deep yellow colour is formed before the end of the time the heating is at once stopped. When cool about 5 c.c. of water are added and the liquid is poured into a 50 c.c. Nessler cylinder, the dish being further washed with about 3 c.c. of water. 1 c.c. of a saturated solution of sodium sulphite is mixed with the liquid and then 10 c.c. of about 6 N ammonia are added while cooling. A brown colour indicates the presence of benzoic acid. Finally 2 c.c. of ammonium sulphide are added, when a deep red colour is produced. The liquid is then diluted with water to 50 c.c. and compared with standards prepared in the same manner. In a particular experiment standards of 3, 5, and 7 mg. of benzoic acid were made. A milk residue to which 5 mg. of benzoic acid had been added indicated about 4·5 mg. on comparison with them.

DISCUSSION.

Mr. F. H. ALCOCK said that, whilst examining a bottle of medicine which was found to contain both sodium benzoate and ammonium chloride, during the process of evaporation the benzoate was dissipated and only sodium chloride with the excess of ammonium chloride remained. This suggested a method for determining the sodium benzoate in milk—the addition of ammonium chloride and submission to steam distillation. The dissociation would take place more readily than ever in acid solution, the whole of the benzoic acid being found in the distillate and in less quantity than 600 c.c. of it. In the authors' process the latter might be concentrated by adding sodium carbonate to fix the benzoic acid before the acid and ether treatment, which would economise the amount of ether. He did not regard as desirable the use of sulphuric acid with sodium benzoate, for fear of the formation of a sulpho derivative which would not be volatilised so readily. He favoured the less destructive phosphoric acid rather than hydrochloric or sulphuric acid.

Mr. LIVERSEEGE, in reply to questions, said the preservative was intended to prevent the milk going sour, and there was wisdom in including the sodium carbonate. The alternative method suggested by Mr. Alcock was certainly interesting.

London Section.

Meeting held at Burlington House, on Monday, February 3rd, 1913.

PROF W. R. E. HODGKINSON IN THE CHAIR.

THE BEHAVIOUR OF PAINTS UNDER THE CONDITIONS OF PRACTICE, WITH SPECIAL REFERENCE TO THE ASPERSIONS CAST UPON LEAD PAINTS.

BY HENRY E. ARMSTRONG AND C. A. KLEIN.

A communication was made to the Liverpool Section of this Society on May 3rd, 1911, by Prof. E. C. C. Baly, on "The Toxicity of White Lead," which became widely known, though not published in the Journal of the Society, through the appearance of accounts of the meeting in various trade journals—notably "The Oil and Colour Trades Journal" of May 6th, 1911, p. 1518 and the Chemical Trade Journal, May 13th, 1911. The final conclusion arrived at in this communication was: "That a definite volatile lead compound is given off in the drying of white lead paint. It appeared to be peculiar to basic carbonate of lead and to explain the prevalence of lead poisoning among painters." We believe that before being presented to this Society, this conclusion had been brought under the notice of the Departmental Committees of the Home Office appointed February, 1911, to consider

When requested, at the time of the appearance of the account of Prof. Baly's work, by a Committee of the London Chamber of Commerce, to consider these statements, one of us forthwith formed the opinion that his conclusion was illogical, unwarranted by the facts and without justification; our experiments show this to be the case.

The opening sentence of the Chemical Trades Journal report:—"Prof. Baly said the experiments which he made were with a view to ascertaining whether it was possible to obtain conclusive evidence as to the toxicity of white paint used by painters"—affords clear indication that Prof. Baly was inclined to assume toxicity, whatever that expression may include. The following sentences show this to be the case:—"Everyone is familiar with the characteristic smell of white lead paint when drying upon a newly painted surface, which was described by painters as the smell of lead. Painters have long ascribed this characteristic smell to lead and it is noticeable that there is no such smell from zinc-white paint. It is well known, too, that while painters do suffer from lead poisoning, only in rare instances is poisoning known among workers in the manufacture and mixture of white lead. It was therefore decided to investigate and to obtain some definite pronouncement with regard to this so-called leady smell."

The argument on which the experiments made by Prof. Baly were based is stated as follows:—"If, as painters insisted, some lead compound was given off in drying white lead, then there would be absorption of light when light passed through the vapour into the spectroscope and so, on these lines, experiments were made."

The question arises, first—have painters long ascribed the smell illogically to lead or logically to lead paint? Then, is it true that they have insisted that "some lead compound" is given off as white lead dries? Was not this last statement a product of the speaker's imagination?

The one serious suggestion which we have been able to find that a volatile compound of lead is given off from paint in drying is made in the Report presented in 1907 by M. Breton to the French Chamber of Deputies. We shall deal with this Report later on.

The reason why Prof. Baly used a complicated photographic method, in the first place, is not far to seek. During the greater part of his career, he has been engaged not in chemical work but in taking photographs of the absorption spectra of substances in solution. He used the method both naturally and because, probably, he wished to show that the very elaborate, costly apparatus at his disposal could be put to practical use.

In the first experiment, a tube was coated inside with "stiff white lead paste containing 7 to 8 per cent. of linseed oil." In the second, "zinc white paint" paste was used; in the third "Purex lead paint." Some light was absorbed in the case of the white lead paint alone.

The experiments were then repeated with the three materials in tubes heated at temperatures varying from 60° to 150° C., photographs being taken at 5° intervals throughout this range; we are told that:—"With zinc white there was no absorption of light up to 100° C., after which there was a small increasing absorption probably due to the linseed oil beginning to vaporise at this point. In the case of white lead, absorption was apparent at 75° C., while purex behaved exactly the same as zinc white."

But as it might be asked, "Why heat the paint?" in the next experiment, "a tube of glass was coated with white lead and placed in a copper tube overnight at 40° C. Upon passing a beam of light through it as before, absorption took place. Another tube smeared with purex treated in the same way showed no absorption."

We are left in doubt what is meant by "white lead" here and when it was that the beam of light was passed through the tube which had been placed in the copper tube overnight. But we are only dealing with a report.

Finally, to test whether a room painted with white lead paint would show the same result (as the tubes) under the spectroscope "two wooden boxes were made 7 ft. long

were allowed to dry in a warm room and then each was photographed with the beam of light passing through. The result was definite absorption with white lead, none with purex."

No definition of "paint" is given. Apparently actual paint was never used but merely mixtures of the solid material and linseed oil, without turpentine.

The conclusion arrived at up to this point by Prof. Baly was that the painter using white lead paint is exposing himself to volatile compounds; this (apart from the fact that painter's paint is something different from Prof. Baly's mixture) is the only logical deduction that he was entitled to make, though by implication his hearers were probably led all through to regard the white lead as an incriminated article, capable of emitting vapour containing lead and presumably poisonous; indeed the implied charge at once follows:—"Having arrived at these conclusions, the point to determine was, what these volatile compounds are. Though this point has not been settled conclusively, enough evidence has been obtained to prove that a definite volatile compound of lead does exist in white lead paint."

Various distillation experiments are then referred to in which distillates were obtained containing lead when white lead had been used but free from lead when purox was substituted for the white lead. No word is said which indicates that any special precautions were taken to prevent the lead from being carried over mechanically or, indeed, that Prof. Baly was in the least alive to the need of taking any precautions to prevent priming.

Finally, the rapid action of litharge on linseed oil is referred to and the opinion expressed that action takes place in a similar manner between white lead and oil, though more slowly, the implication being that the primary volatile lead compound is produced because "while grinders and mixers rarely suffered from lead poisoning, painters frequently did, owing to the fact that the white lead paint was kept eight to nine months, during which time the reaction took place."

In opening the discussion, Mr. Carey, the Chairman, said "that Prof. Baly had made a speciality of spectroscopic work and his contribution that evening had shown them one of the uses to which the spectroscope could be put." We should prefer to say *misuses* rather than *uses*.

The following remarks made by two medical men present at the meeting, showing the impression produced, are of interest in more than one particular:

"Dr. Collis* said that doctors always argued that the poisoning of painters must be due to dust, while the painters themselves always insisted that it was due to the leady smell, as they called it, from white lead paint. Professor Baly had shown that the painter was right after all. He always thought that chemists could help doctors more than had been the case up to the present. His own personal opinion was that rather too much was made in these days of microbes. It was true that microbes did a great deal of damage, but he thought that in many cases it was due to the vitality of the human system having been previously lowered by other means before the microbes got to work."

"Dr. Buchanan,† a toxicologist, said that one of the surest indications of lead poisoning was the alteration in the corpuscles of blood which took place half an hour after inhaling. He mentioned that he had drawn the attention of one of the district medical officers to this fact and he had let his daughter examine the blood of patients who came under his notice. After a time his daughter, who was quite healthy, showed signs of lead poisoning by (on examination of her) red blood corpuscles. The medical officer was at a loss to understand this, until it transpired that some painting had been done at her home.

It is evident that Prof. Baly paid no attention to existing knowledge of the behaviour of drying oils—to the well-known fact that the drying process involves more or less oxidation of the oil and that volatile products are formed; also that he in no way took into account the use of turpentine or other volatile liquids in thinning paints and that the vapour of these is at once given off rapidly from the painted surface: even Drs. Collis and Buchanan, the medical men present, seemed to be unaware of this latter circumstance.

Three questions were before us when we commenced our experiments:—

1. The possible effect of the various constituents of paints taken singly; in other words, whether the symptoms supposed to be characteristic of lead poisoning were in reality due to lead.

2. The extent to which volatile substances were produced at any stage either during the preparation of lead paints or during their use by painters.

3. Whether volatile lead compounds were producible or produced in the manner Prof. Baly had indicated.

1. It is well known to the chemist that the compounds of lead generally and also the fatty oils used by painters are not volatile in any ordinary sense of the term. The few volatile compounds of lead, such as the tetraethide ($PbEt_4$), that are known are altogether peculiar substances and there is no probability that such are formed from white lead and oil. But turpentine is well known to be a very volatile substance and a powerful irritant of the skin; those who have worked with it much are well aware that it produces headache and that it also affects the stomach; different persons, however, are sensitive to its action in very different degrees and painters, as a rule, seem to become accustomed to it early in their career. Russian turpentine is far more active than either French or American turpentine—probably owing to the presence of easily volatile products of destructive distillation.

We were led at the outset of the inquiry to make the suggestion that some at least of the symptoms ascribed to lead poisoning were to be attributed to the turpentine in the paint—especially the effect on blood corpuscles commonly regarded as symptomatic of lead poisoning.

It is somewhat remarkable that, apparently, this point has escaped the notice of the medical experts. Dr. K. R. Goadby, one of the authorities on lead poisoning, has made special experiments to test the validity of our contention which have led him to conclusions in entire agreement with our suggestion.

Dr. Kenneth Goadby* has found that animals subjected to the vapours given off from white lead paste at an elevated temperature, viz., 50° C., were quite unaffected after over 300 hours' exposure, whilst those exposed to the vapours produced at ordinary room temperature from a surface painted with any paint containing turpentine suffered from the outset. Whilst he was unable to distinguish between the physiological effects produced by paints containing white lead, basic sulphate of lead, zinc oxide or lithopone, it was obvious that the animals suffered through the agency of a common cause; further experiments showed that the ill-effects observed were due to turpentine vapours and could be reproduced in other animals by subjecting them to turpentine vapour alone.

In determining whether and to what extent volatile products are formed from linseed or other oils and the ordinary materials used in making paints, we have substituted for the very complicated and expensive apparatus used by Prof. Baly a very simple and inexpensive test which it is open to every one to use. This has the advantage of being a physiological test comparable with that afforded by the human subject, comparable even with the blood corpuscle, a test, moreover, the result of which cannot well be misinterpreted—the leaf of the common shrub the *Aucuba Japonica* or spotted Japanese laurel. When the leaf is exposed in an atmosphere of any volatile substance, it blackens more or less rapidly, as the vapour which enters through the stomatal openings of the under surface rapidly induces the interaction of a glucoside (*aucubin*) present in the leaf and a corresponding enzyme, the immediate product of change being a substance which undergoes alteration in a manner not yet understood into an almost black substance.

We believe the test is likely to prove of special value in examining oils to be used in making paints. All that

* A Medical Inspector of the Home Office and a member of both the Departmental Committees referred to.

† Professor of Toxicology, University of Liverpool.

* Lead poisoning and lead absorption, Legge and Goadby, p. 108, Arnold, London, 1912.

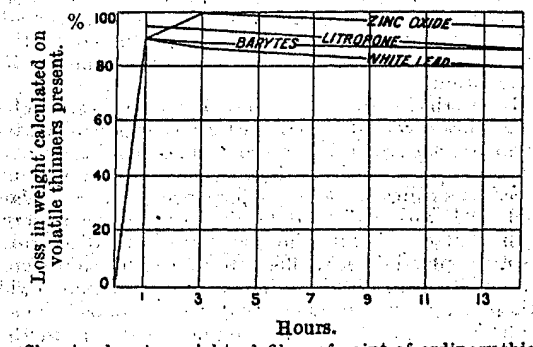
is necessary is to shut up the leaf along with, though not in contact with, the material to be tested, in a large test tube, bottle or jar; in order to hasten the action, the charged vessel is best placed in an incubator at about blood temperature (35—37° C.).

Nothing happens when the *Aucuba* leaf is exposed during 24 hours in presence of either dry white lead or of any of the solid materials used in paint making or of any of the oils used in making paint; but the leaf blackens rapidly in the presence of turpentine, the effect being visible often after a few minutes and the blackening complete usually within an hour. The leaf varies in sensitiveness, being most sensitive during the growing period. We are confident that all the liquids which can be used in thinning paint would act similarly. Recently we examined several samples of turpentine substitute thinners now on the market and found all to be extremely active.

The fact that turpentine and similar liquids produce the effect so rapidly is of special significance in connexion with the effects sometimes observed in newly painted apartments. We believe that the vast majority of complaints that are made against paints as having caused inconvenience or serious effects are simply and solely due to this cause alone. It also follows that the one necessary precaution to take is not to risk exposure to the vapour; as the turpentine evaporates rapidly from a painted surface it is not difficult to avoid being subjected to its influence. Those painters who are specially sensitive should not be allowed to undertake work (flatting) in which much turpentine is used.

To test the behaviour of paints in drying, a series of paints were made up so that each contained the same quantity of turpentine. These were then applied to glass and the weight determined at intervals. That an immediate decrease in weight takes place owing to the rapid evaporation of turpentine is obvious; and the induced drying effect is clearly shown in the following curves:—

CURVE I.

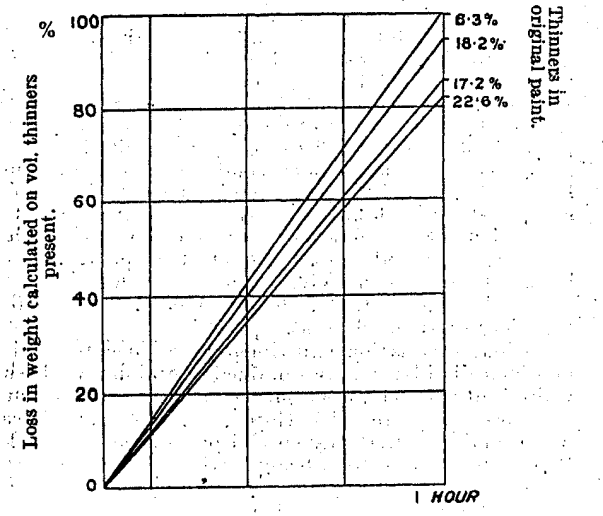


Showing loss in weight of films of paint of ordinary thickness—paint applied on glass. The drying effect is seen. Paint contained 20% vol. thinners.

It appears that practically the whole of the turpentine is removed after a period of one hour and that there is little difference in the behaviour of different paints, whatever the base; obviously the effect of the turpentine is the same, whatever base be used. It is to be noted that most of the substances introduced as substitutes for white lead require a larger proportion of thinners. We have examined eight of the most advertised substitutes on the market. These are sold either in paint or paste form and vary in volatile thinners from 5—22 per cent. All these thinners are toxic to leaves.

2. When an *Aucuba* leaf is exposed over a mixture of white lead and linseed oil, it sooner or later shows signs of being affected, black spots appearing here and there; after 2 or 3 days black patches are usually visible or it may be nearly black all over. When boiled linseed oil is used, this effect is produced more rapidly. Of course, the leaf is not so immediate a test of the presence of vapour as the spectroscopic test used by Prof. Baly; it is, however, sufficiently rapid and not only has the advantage of being both simple and practical but is of special value, as it is a cumulative test which affords ocular demonstration of the rate at which and the extent to which volatile products are being given off from the substance or mixture to which it is exposed. The behaviour of the *Aucuba* leaf and also of the ordinary laurel leaf when exposed to vapours has been fully discussed by one of us in conjunction with E. F. Armstrong.*

CURVE II.



Loss in weight of paint films due to volatilization of thinners. After one hour paints began to dry so that volatilization loss is balanced by drying. The above are four well-known white lead substitutes.

We may here state that all the materials used in our experiments were of good commercial quality as determined by analyses before use. The white lead used was of English manufacture—both stack and other process products; the oxysulphate used was in part of French and in part of English manufacture and consisted entirely of basic sulphate of lead unadulterated with barium sulphate in the manner now practised in England.

We have exposed leaves, at blood heat, in presence of a great variety of mixtures of solid materials with linseed oil. In all cases some effect has been visible sooner or later, whilst leaves exposed simply over water have undergone no visible change during the same period. In the case of mixtures containing either white lead or sublimed oxysulphate of English or French manufacture, blackening has sometimes been complete after 3 or 4 days; but leaves exposed over mixtures made from either lithopone or natural barytes or zinc oxide free from lead became more or less spotted in the same time; even lime and baryta have been found to hasten the production of the vapours. Eventually the leaves exposed over oil alone have shown signs of blackening, proving that the oil is slowly undergoing oxidation; leaves exposed over boiled oil blacken much more readily than those exposed over raw oil and when boiled is substituted for the unboiled oil in any of the mixtures the blackening takes place more rapidly.†

* The function of hormones in stimulating enzymic change in relation to narcosis and the phenomena of degenerative and regenerative change in living structures. Roy. Soc. Proc., 1910, **82**, 588. The function of hormones in regulating metabolism, Annals of Botany, 1911, **25**, 507.

† *Nature of the volatile products produced from linseed oil.* It has long been known that considerable amounts of volatile products are formed in the process of drying linseed or any other drying oil. Genthe (Zeits. f. ang. Chem., 1906, **19**, 208) states that the loss amounts to 15 per cent. in the case of linseed oil drying at ordinary temperatures. Reid (Journ. Soc. Chem. Ind., 1898, **17**, 75) records that in the manufacture of linoleum (where large quantities of linseed oil are oxidised) a gain of only 10 per cent. is observed and ascribes the difference between this gain and the theoretical gain to loss of volatile products. We have examined solidified oil obtained from the volatile products given off on boiling oil together with litharge, the samples being collected from areas where mechanical spraying was impossible; we were unable to find lead in these. Oil boiling is carried on at elevated temperatures and therefore the conditions are such as would be favourable to the formation of volatile organic lead compounds if such were possible.

It is to be noted that Baly has also examined such products and has failed to find lead present.

The behaviour of zinc oxide is variable; sometimes the leaves blacken rapidly over mixtures of this substance with linseed oil. The differences observed may be ascribed to the presence of lead or perhaps of manganese in varying amounts. It is well known, that, excepting the New Jersey brand, zinc oxide made from the ore generally contains from 1 to 5 per cent. of lead (as oxy-sulphate); that made from spelter is usually free from lead. It may be noted that certain standard English specifications specify that zinc white shall not be blackened by sulphuretted hydrogen.

Mixtures of linseed oil with the various commercial driers all affect the leaves more or less rapidly; we therefore think that the "Aucuba" test is one that may prove to be of value in testing the efficiency of driers.

Nor is linseed oil peculiar in this respect; cornflower oil, crude and refined soya bean oil, menhaden oil and even olive oil give off vapours moderately rapidly, when mixed with either white lead or driers or both, on exposure to air; castor and China-wood oils are more slowly affected. There is no doubt that any oil that will dry and can be used in paint will yield volatile products during the process of drying.

3. Taking into account what is known of the compounds of lead, it was inconceivable that the vapours given off during the drying of lead paints should contain lead. From the experience gained from a large number of experiments we have made to test whether lead is volatilised as Prof. Baly has asserted it is, we are able to state positively that lead cannot be found in the distillate from the distillation either of white lead or of basic sulphate of lead *when effective precautions are taken to prevent the contents of the distillation flask from being carried over mechanically into the distillate.* It is astonishing, however, how easily priming takes place when a mixture of oil and white lead is heated and how difficult it is to prevent particles of solid from being carried over when a mixture of oil with any solid substance—not white lead alone—is subjected to distillation in a current of steam. Oxy-sulphate (Purex), in our experience, is just as "volatile" as white lead.

We have tried in many ways to prevent this priming effect and have found the most effective preventative to be the use of a length of half-inch block tin tubing, bent at an acute angle about one foot above the distilling flask, as connecter and condenser, in the manner advocated by Dr. Bernard Dyer for the determination of nitrogen by the Kjeldahl method.

When a mixture of white lead with oil is heated, the basic carbonate is decomposed and both steam and carbon dioxide are given off: solid particles are easily carried forward in the spray that is formed by the bursting of the bubbles as the gas escapes.

When the distillation is effected under reduced pressure, this effect is even exaggerated. When basic sulphate of lead is heated, no gas is produced and but little water is given off, so that there is far less priming.

It is necessary here to point out that no such spraying effect or mechanical separation of particles as is observed in distillations can occur during the drying of paint under the conditions of ordinary practice and therefore these experiments have been carried out under conditions much more rigorous than obtain in practice.

A proof of the inefficiency of glass traps in preventing priming is afforded by experiments made with the apparatus shown in Fig. I. A mixture of oil and the lead salt to be distilled in a current of steam having been put into a flask about 800 c.c. in capacity, steam was passed into the mixture and afterwards through flasks 1 and 2 into the upright tower and thence through a condenser.

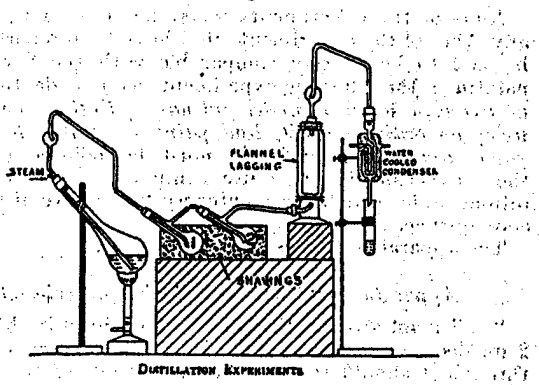


FIG. 1.

Experiments were made using (1) white lead and (2) litharge, linseed oil and lead acetate being added in each experiment. No lead was found in the final distillate but the contents of the first receiving flask contained lead, whilst the second receiving flask and the tower were free from lead.

The presence of lead in the first receiver flask could be due to one or both of two causes—(1) to a volatile lead compound soluble in water and volatile in steam but not volatile at the temperature of No. 1 flask; and (2), to the spraying over of the lead compound.

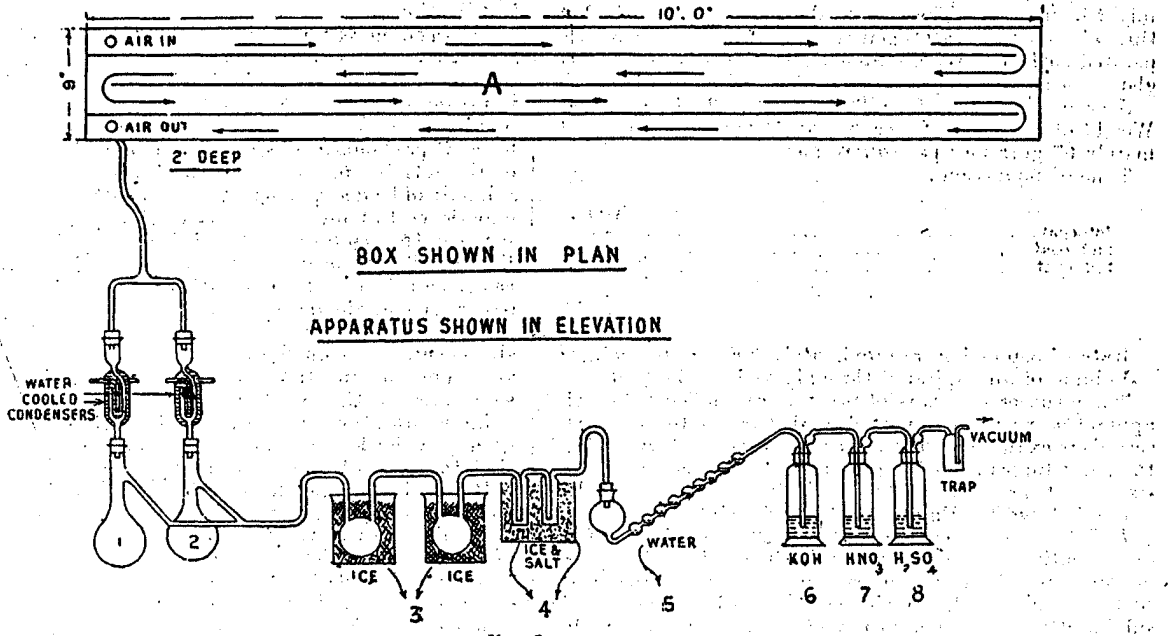


FIG. 2.

In order to decide between these alternatives, the experiment with litharge was repeated with the following alterations:—

(1) Flask No. 1 was heated by a boiling water bath so as to drive off any volatile lead compound in solution, it being obvious from the previous experiment that if a volatile compound were formed it was volatile at this temperature.

(2) Flask No. 2 and the tower were exposed to the air.

The distillation was continued during half an hour. On examining the distillates, lead was found in the first flask but not a trace was detected either in the second flask or in the tower or in the distillate—showing that lead had been carried from the distillation flask mechanically into Flask No. 1 and that, although the liquid in this was kept boiling, the lead compound travelled no further: proof was thus obtained that the lead compound was sprayed over from the distillation flask.

Painting Experiments.

None of the experiments so far described nor, indeed, any other of the experiments that have been reported, can be said to be exactly comparable with the practice of painting; the following experiments were made, therefore, *to ascertain whether, under ordinary painting conditions, using an ordinary white lead paint, a volatile lead compound could be isolated.* It must be pointed out that these experiments are quite comparable with the conditions under which the painter works and are of value in consequence.

The apparatus used is shown in Fig. 2.

Apparatus used in paint drying experiment.

"A" is an air-tight box, 10 ft. long by 9 in. broad by 2 in. deep, arranged so that the air which was aspirated through it should travel over the surface of the box by means of channels, the air thus travelling the length of the box four times, as shown. The box was fitted with a glass top, in order that the paint should dry under normal conditions as regards light. This feature has been omitted in all other reported experiments, although the important influence of light in the drying of paint is well known. The joints between the top of the channels and the glass were made by laying thick walled rubber tubing on the top side of the partitions and tightly screwing down the glass cover, so as to render it air-tight, thereby compelling the air to travel through the 40 ft. of channel. The box was painted with an ordinary linseed oil and turpentine paint and at once closed; aspiration was then commenced, the air passing through the various devices shown, in order to absorb, if possible, any volatile compound which might be formed. The outlet tube was fitted into the box through a cork, so arranged that the tube was above the painted surface. Where possible, all joints were of fused glass; otherwise they consisted of paraffined cork.

Area of painted surface, 20·80 sq. ft.=1·94 sq. metres. Weight of paint used for each coat, 130 grammes, approximately 67 grammes per square metre.

Time of aspiration:

	hours.
1st coat	48
2nd coat	12
3rd coat	18
	78

Rate of aspiration, approximately 300 c.c. per minute.

Volume of air aspirated through, at least 1400 litres.

Three successive coats of paint were applied before the apparatus was disconnected and the contents of the scrubbers examined; therefore the apparatus had received the paint fumes from 390 grammes of paint covering, as a single-coat, an area of 62·5 square feet.

Flasks 1 and 2. Empty:—odour of paint.

Bulb 3. Contained 5 c.c. of colourless liquid, smelling of turpentine. When boiled with nitric acid, this became yellow; on adding ammonia, there was no change; on adding acetic acid, no change; colourless when cold; sulphuretted hydrogen produced very slight straw discolouration.

Trap 4. 3 c.c. colourless liquid, smelling of turps. Tested as above, very slight straw discolouration; quantity, if any, too small to afford a positive result.

Washer 5. Colourless liquid—free from lead.

Wash bottle 6. Yellow liquid; crystals on bottom; soluble in water. Sweet ester-like smell. Free from lead.

Wash bottle 7. Brownish-yellow liquid. Evaporated to dryness and ignited. Left a large quantity of carbonaceous residue. Extracted with nitric acid—free from lead.

Wash bottle 8. Very pale yellow—free from lead.

Conclusion: Volatile lead compounds are not produced in appreciable quantity when a freshly-painted surface is dried under normal conditions.

The experiment was repeated but without obtaining any indication of lead.

Effect of age on white lead ground in oil.

Baly has suggested that the formation of volatile lead compounds in white lead and oil takes place during the period of nine months. This suggestion was based on indirect evidence and was rendered necessary by the fact that workers engaged in the grinding of white lead do not suffer from lead poisoning. If, however, the volatile products were formed at once the occupation would be most deadly, as the temperature of grinding is often higher than that at which Baly has stated volatile lead products are produced.

In order to investigate this suggestion experimentally we examined a sample of white lead paste ground in September, 1907, which meant a period of 51 months between time of grinding and examination; the results obtained were exactly the same as those obtained on using new white lead and linseed oil, showing that it is impossible to detect any volatile lead compound in white lead paste which has been stored during 51 months, so that on experimental grounds the suggestion is unsound.

Further, we have compared the rates of blackening of leaves exposed over white lead paste 1 day, 9 months and 55 months old and can find no difference.

Professor Baly's second communication.

A second communication on the toxicity of white lead paints was brought before the Liverpool Section of this Society on March 13, 1912, and was published in the Journal issued on June 15, 1912, 31, 515. No word of reference is to be found in this to the previous communication—not the slightest apology is offered to white lead for the slur previously cast upon its character but it is subjected to a further damaging accusation: again, we think without justification.

The opening sentences of this second communication are somewhat more guarded than those of the earlier paper—moreover an interesting indication is given of the true inwardness of the object Professor Baly had in view in making his experiments, as he states: "The matter was brought particularly under my notice during a discussion of the relative merits of the basic carbonate and basic sulphate of lead as pigments. Even without any previous experience I at once detected a most decided difference between the smell of the two substances when ground in linseed oil. It occurred to me that this matter could easily be put to a strict scientific test and in the present paper are contained the results of some experiments I have made in this direction. It may safely be said that any statements as to smell and even as to cases of poisoning are somewhat unsatisfactory unless there is forthcoming some proof of the exhalation of poisonous vapour by the paint in question. It was to investigate whether or no any volatile and poisonous emanations truly occur that the present work was undertaken."

It is a little difficult to understand how the relative merits of carbonate and sulphate as *pigments* could be determined by the study of vapours given off from mixtures of the substance with oil: and the logic of the statement—"I at once detected a most decided difference between the smell of the two substances when ground in linseed oil"—is not easily perceived: what smell has to do with the merits of a substance *as a pigment* is not clear.

The spectroscopic observations described are obviously those described in the first communication. But at the end of the account that is given of them, we read :—"It may be of some interest to record the fact that the smell of the glass tubes after they had been heated in the above experiments was singularly nauseating, and in the case of the tubes containing the white lead the vapours produced certain specific symptoms such as lassitude and severe localised headache followed by diarrhœa."

Now it is well known that the smell of an expiring tallow candle is "singularly nauseating," yet we put up with it occasionally and are unhurt. Professor Baly must have gone very much out of his way to make himself ill and one would like to know exactly how he did it. The value of his evidence depends entirely on this—on his sensitiveness to impression and on proof being given that when his health was disturbed the said vapours were the actual and sole factors of the disturbance : their average effect rather than their Baly effect should have been determined—he may well have been subject to mental impressions during the inquiry.

We are interested in having our observation (that no volatile compound containing lead is given off on heating white lead with oil) confirmed by Professor Baly in the positive way in which it is confirmed in this second communication. As the following statement shows, he is uncompromising in his admission but he might have had the candour to confess that he had repeated his experiments because of our failure to confirm his results.

"Comparative tests were made with white lead and basic sulphate and in the earlier experiments distinct evidence seemed to be obtained that there was produced a small quantity of a volatile lead compound in the case of the white lead. More recent experiments did not confirm these results and therefore it was concluded that the lead in the earlier experiments must have been mechanically carried over in the form of carbonate. In order to obtain more definite evidence as to the question of volatile lead compounds, about 4 lb. of the stiff paste of white lead and linseed oil was heated *in vacuo* by an oil bath and the products condensed in a vessel cooled by liquid air. On allowing the temperature of the receiver to rise, a considerable quantity of gas was evolved, leaving about 30 c.c. of liquid. This liquid contained a large quantity of water and was tested for lead but no definite evidence of the presence of this metal was obtained."

The lead bogey being perforce thus cast aside, the nauseous vapour bogey is now dragged upon the scene.

"It was found that the gaseous product possessed an indescribably nauseous odour and was undoubtedly poisonous, similar results being produced as those already described. This experiment was repeated with basic lead sulphate but little or no distillate was obtained."

Experiments are then described to establish the self-evident proposition that when a hydrated substance is heated vapour of water is given off, and that this does not happen when no water is present, as in the case of basic lead sulphate.

Finally we read : "I cannot claim that the above experiments represent the last word upon the subject but I do feel that as far as they have gone they establish the fact that a poisonous volatile substance is given off paints made with white lead or red lead. It seems to me to be a necessary conclusion that we must recognise the existence of a source of poisoning in connexion with painting that is to be differentiated from lead poisoning proper. The symptoms described in the earlier portion of this paper were experienced by me both with the vapours from the manganese dioxide and oil mixture so that it would seem impossible to attribute them to lead poisoning. These symptoms, my experiments shew, are doubtless due to the evolution of unsaturated aldehydes and these are given off by any paint containing oxidising agents, white lead or red lead. The cases of poisoning which have been noted amongst people inhabiting rooms freshly painted with white lead would seem therefore to be due to these unsaturated aldehydes and not to be true lead poisoning.

"It is perfectly possible to minimise the amount of this poison by utilising either basic lead sulphate or zinc white and by using as little drier as possible : I say this with the more confidence, because, of the white paints, white lead was the only one that gave at ordinary temperatures a measurable amount of the aldehyde in my experiments. For this reason the conclusion must be drawn that danger attends the use of white lead paints.

"The same must be said of red lead, for it seems that the poisonous volatile compound is even more readily given off by this substance."

It is to be noticed that the nauseating vapours were only obtained by heating the mixture of white lead and oil to 60°—65° and that apparently similar vapours were obtained when Purex and zinc white were used, though only at higher temperatures. Such results are clearly in no way comparable with those obtained in practice when paint dries at atmospheric temperatures—no one thinks of describing the smell then obvious as singularly nauseating.

Objection may be taken, on similar grounds, to the comparative experiments in which the relative amounts of silver reduced in equal times by the vapours given off from various mixtures were determined.

The term "poisonous volatile compound" after all is a purely relative expression. Chloroform is a most poisonous volatile compound—yet people are daily, of set purpose, subjected to its vapours and, as a rule, are but temporarily affected by it. Ammonia has extraordinary toxic powers and yet it is used by women all the world over as smelling salts and in recovering them from fainting fits. Every known volatile substance is more or less toxic. Cheese is regarded as a valuable food all over the world, yet at times, in some people, it produces considerable stomach derangement. Clearly the poisonous vapour bogy has been manufactured by Professor Baly as a means of escape from a difficulty in which he had placed himself by discovering volatile lead where there was no lead and he has used it as a stone to cast at white lead.

As a matter of fact, he has adduced no more evidence in his second communication that white lead *under conditions of practice* gives rise to an amount of vapour capable of producing effects such as would justify the use of the term poisonous than he has that lead itself is volatilised.

In condemning white lead, moreover, he has condemned paints altogether. As Mr. Morris said in the discussion :—"As regards the use of dryers, it was necessary for the paint to dry quickly. How could they get away from the commercial aspect of the case by using less dryers or none at all ?"

If a paint is to be of any practical use, it must dry : the nauseous substances of Professor Baly will arise : but every one connected with the industry—every painter throughout the country—knows full well that the rate at which the change takes place is so slow, the quantity of vapour given off so slight, that it is quite easy, in practice, to avoid ill effects. It is only necessary to ventilate a little and to give the paint time to dry.

Paints cannot be made without oil and cannot well be applied unless thinned by a volatile liquid ; and some drying agent must be present in them. Whatever volatile liquid be used to thin a paint, it will be capable of producing effects such as turpentine produces—in Baly language, it will be poisonous. But it is perfectly well known that it is possible by very simple precautions to prevent any serious effects arising—those painters who, like Professor Baly, are specially sensitive to the influence of vapours must not be allowed to flat large surfaces in closed apartments.

And we must set on the other side the hygienic value of painting with an oil paint containing a drying agent and a penetrating volatile substance such as turpentine, to which Dr. Goadby, we believe, has drawn special attention ; no more effective means—probably no such effective means—of destroying micro-organisms can possibly be devised. If a room be well washed down, then rewhitewashed and repainted, especially if it be shut tight while the paint is still fresh and left for the vapours that are given off—both those of turpentine and those of the Baly bogey—to act antiseptically, the chance of organisms surviving will be very small. None of the conventional recognised methods of disinfecting can be so effective.

M. Jules-Louis Breton's Report.

"Rapport fait au nom de la commission de l'hygiène publique chargée d'examiner le projet de loi, adopté par le Sénat, sur l'emploi des composes du plomb dans les travaux de la peinture en bâtiments." Paris, Imprimerie de la Chambre des Deputés, Motteroz et Martinet, 7, rue Saint-Benoit, 1907.

This report is to be regarded as of special importance, owing to the action taken by the French Government in legislating prospectively against the use of white lead even for outside painting purposes. Probably everything that can be said against white lead is to be found in its pages. We are concerned only with the chemical evidence adduced by M. Breton himself, by M. Trillat and by MM. Heim and Hébert.

Before referring to these, we may mention that it is on record that the great Stas, when questioned, in 1855, whether the symptoms sometimes shown by delicate persons, after living in a room recently painted with white lead, could be due to lead poisoning, is said to have replied that experience showed that a recently painted room could be inhabited with impunity.

In giving evidence before the Chamber of Deputies, in 1903, Prof. Armand Gautier expressed the opinion that persons inhabiting rooms painted with white lead do not run any risk, as lead paint does not emit either emanations or dust.

M. Breton (Report, p. 334), in objecting to the removal of paint by burning off, which he speaks of as provoking "la production d'émanations plombiques," refers to an opinion expressed by M. Gautier to the effect that painters are subject to poisoning from this cause "parce qu'ils ne peuvent pas se soustraire *aux poussières* plombeuses ainsi produites." It is noteworthy that he does not suggest that lead is ever *volatilised* during the operation.

M. Breton's experiments.—M. Breton gives details (Report, p. 335) of experiments made by himself, in 1903, which he considers prove that a volatile compound of lead is produced during the drying of lead paint. He appears to have arranged a series of freshly painted metallic boxes concentrically under a bell jar, through which he then aspirated air, this air being afterwards bubbled through a 10 per cent. solution of sulphuric acid. At the end of a day lead was detected in the acid. M. Breton explicitly states, however, that the quantity of lead present was "*extrémement réduite* et que les réactifs ordinaires du plomb ne peuvaient la révéler." He based his assertion that lead was present on the use of Trillat's agent—which is not specifically a test for lead.

M. Trillat, at his request, repeated the experiment but did not confirm the result. To this M. Breton objects that M. Trillat had only painted the interior of the bell jar "au lieu d'employer notre dispositif de boîtes en chicane qui nous donnait une très grande surface d'émanation!"

He then proceeds:—

"Cette disposition opératoire différente explique parfaitement la différence des résultats obtenus; car, nous le répétons, nous n'avons pu dans notre expérience constater l'entraînement que de traces infinitésimales et presque indosables de plomb et la diminution, d'ailleurs considérable, de la surface d'émission devait nécessairement rendre impossible cette constatation.

"Mais, comme nous avons renouvelé à plusieurs reprises, en prenant toutes les précautions possibles, et en contrôlant soigneusement tous nos réactifs, l'expérience ci-dessus décrite et que toujours nous sommes arrivés au même résultat, nous pouvons assurer formellement que, quoique très faibles, ces émanations se produisent réellement.

"Nous avons d'ailleurs varié notre dispositif en faisant barboter l'air dans la peinture de céruse contenue dans un ballon de verre et avons pu constater de cette manière l'entraînement du plomb en utilisant simplement les réactifs ordinaires, acide sulfhydrique ou monosulfure de sodium."

With reference to this last experiment, we have no hesitation in asserting that the lead detected by M. Breton was carried forward mechanically; we have failed in obtaining evidence of the presence of lead, when the precaution was taken of preventing any spray that is formed as the bubbles burst at the surface of the paint from being carried forward by interposing a scrubbing flask between that containing the paint and the receiving flask. And, as we have already stated, we have been unable to detect lead in air aspirated during hours through a box exposing a freshly painted surface which we imagine was far in excess of that exposed in M. Breton's experiment with *boîtes en chicane*.

Heim and Hébert's experiments (Report, p. 339).—In 1907 MM. Heim and Hébert carried out a series of experiments with the object of detecting and measuring the amount of lead in the atmosphere of workshops where white lead was used. Ultimately they devised a method based on the use of Trillat's agent.

In examining the air of workshops, the air was drawn through a plug of cotton wool (*ouate*). They were struck by the fact that they very often found traces of lead in their absorption apparatus, even after such filtration of the air; they therefore assumed that some portion of the lead in the atmosphere was in a state of vapour and capable of passing through the filtering plug without being caught by it. No proof was sought for that a larger or more tightly packed plug, if not a series of plugs, would be effective.*

They made various experiments, in which air scrubbed by passing through two vessels, one containing sulphuric acid, the other potash, was passed through a long tube 1–2 cms. in diameter containing the material to be tested. When the material was a powder, the two ends of this tube were plugged with cotton wool. The air from the tube, after passing through a U tube "bourré de coton bien serré, assurant sa filtration parfaite," was conducted through a Gautier absorber containing about 10 c.c. of dilute sulphuric acid. The rate of passage was from 3—4 litres per hour and the experiment was continued until 100 litres had been passed through the tube.

In the experiments with litharge and white lead, the tube contained a mixture of 150 grammes of emery with 11 grammes of the former and 15 grammes of the latter. The amount of lead carried forward in 100 litres of air was estimated to be as follows:—

	Milligrammes.
White lead at 15°—20°	0·15, 0·20, 0·12
Litharge at 15°—20°	0·01, 0·01
at 100°	0·01, 0·01

We venture to think that if lead was carried forward, of which the experiments afford no actual but merely inferential proof, it was carried forward in the form of dust. On making experiments in the manner described by Heim and Hébert, using sulphuretted hydrogen as the test for lead, we have found that dust may be carried forward in the air stream unless particular care be taken in packing the cotton wool plug tightly.†

Trillat's test for lead.—This test is based on the fact that when the compound formed by condensing formaldehyde and dimethylaniline is subjected to oxidation, it is converted into the carbinol $HO.CH(C_6H_4{\cdot}NMe_2)_2$, which gives coloured salts with weak acids, though those with strong mineral acids are colourless. The use of the diphenylmethane base as a test for lead depends on the fact that it is oxidised and converted into the carbinol by lead

* The difficulty of constructing efficient filters to remove lead dust from air is recognised in the report of the Home Office Committee on the use of lead in potteries.

†It is of interest that Baly was unable to find any absorption took place when light from a cadmium arc was passed through tubes containing dry white lead and that this observation is cited by him to show that even spectroscopic methods allow of no volatilization of white lead being detected at ordinary temperatures.

Finally, in the Report of the Medical Inspector of Factories, contained in the Annual Report of the Chief Inspector of Factories for the year 1911, Cd. 6929 page 210, we find the following:—

"Experiments were carried out in the laboratory of a lead smelting works in London to determine the temperature at which lead fumes arise from the surface of open baths of molten lead. They showed that unless pure lead is heated to about 500° C. and at the same time stirred, no appreciable fume comes off. . . . When a bath of molten lead is not stirred at all it can be heated to over 740° C. without finding oxides in the air."

This statement is not in agreement with the figures of Heim and Hébert who claim to have shown that lead volatilises at ordinary room temperatures.

peroxide; but it is acted upon equally well in the same way by manganese peroxide and not a few other oxidising agents.

To use the test, the solution of sulphuric acid supposed to contain lead is evaporated to dryness in a small dish and a drop or two of a solution of sodium hypochlorite is added to convert the lead sulphate into the peroxide; according to Trillat, the excess of the hypochlorite is removed either by washing or by calcining. The agent is then added to the residue in the dish. The presence of lead is indicated by the appearance of a blue colour, either at once or on warming. Trillat recommends the use of acetic acid in preparing the agent but there are objections to this and Carney has proposed to substitute citric for acetic acid. We can support his recommendation.*

We are in no way satisfied with the test as one suitable for the detection of minute amounts of lead, especially on account of the difficulty of removing any excess of hypochlorite by washing; obviously calcining is out of the question, as it is likely to decompose lead peroxide. In our hands the results have been somewhat irregular and we are not inclined to rate it as much more if at all more sensitive than the sulphuretted hydrogen test.

The results obtained by Heim and Hébert do not carry conviction. In the first place, no blank experiments are quoted showing that they had tested all the materials they used, though it is to be supposed that they took this precaution. They state that after passing 100 litres of air over lead filings at 18° C., they found as much as 0·5 mgrm. of lead to be volatilised; when, however, the lead was heated to its melting point (335°), the amount volatilised was only 0·4 mgrm. and fused type metal (m.p. 260°) and plumber's solder (m.p. 224°) gave only 0·2 mgrm. If lead volatilises under such conditions at all, it does not seem probable that there would be no increase in the amount volatilised on raising the temperature from 18° to over 300°; the difference is scarcely accounted for by Heim and Hébert's contention that the surface exposed is greatly reduced by the fusion of the metal. We are inclined to think that the lead was carried forward as dust, as on repeating the experiment, using a tightly packed plug of cotton wool, we have not been able to detect lead by the sulphuretted hydrogen test.

Trillat's experiments (Report, p. 344).—M. Trillat's experiments consisted in placing four Petri dishes at different heights under each of three sterilised bell jars of 10 litres capacity; these dishes contained Raulin's fluid inoculated with a culture of *Penicillium glaucum*. Nothing else was put under the one bell jar but the second had in it a dish containing about 50 grammes of powdered white lead and the third one containing a paste of white lead and linseed oil. In the case of the blank bell jar, growth set in at the beginning of the third day; in the second, containing dry white lead, a slight retardation was noticeable; in the third, the retardation of the growth of the organism was obvious.

In a second set of experiments, *Aspergillus niger*, a more sensitive organism, was substituted for *Penicillium*. The experiment began on Jan. 15th; on Jan. 19th a few colonies were seen in the blank bell jar and in that containing dry white lead, though they were slightly less numerous and less compact in the latter. No growth had set in under the third bell jar at the end of 15 days, when the cultures under the two other jars were fully developed. An experiment carried out with oil alone showed that this had no influence in retarding the growth of the organism. It was also found that a paste made by mixing white lead with water had no appreciable effect.

Precisely similar results were obtained by Dr. Marie (Report, p. 346), using *Ebert's bacillus*. This observer also tried the effect of a mixture of zinc white and oil and found that the growth of the organism was "plus net et complexe" than that in presence of the mixture of oil and white lead, "rappelant celui de la première culture en présence d'huile pure mais moins florissante bien que nettement plus vivace qu'avec le plomb."

It is obvious, however, that such results in no way justify the conclusion that Dr. Marie draws when he says: "elles montrent l'action d'arrêt *des vapeurs métalliques* par rapport aux phénomènes organiques vitaux élémentaires."

The very slight initial effect observed by Trillat, in a single case, on exposing organisms in presence of white lead alone, is of no significance in view of the irregularities often manifest in such experiments.

M. Breton quotes an experiment (Report, p. 348) made with a guinea pig, which was killed by exposure to air aspirated through a vessel containing a mixture of 300 grammes of white lead, 100 grammes linseed oil and 25 grammes of turpentine.

After calling attention (Report, p. 349) to the opinion expressed by MM. Riban and Bouchardat that turpentine exercises toxic effects, M. Breton then states that he had exposed a guinea pig in a precisely similar manner to the vapours given off from a mixture containing zinc white in place of white lead and that no ill effects were produced.

Dr. Goadby, who has carried out an exhaustive series of experiments with various bacteria, similar to but far more extensive than those made by MM. Trillat and Marie, has failed entirely in detecting any effect in the case of organisms exposed in presence of white lead alone. He has also shown that whether the paint used be made from white lead, zinc white or lithopone, the vapours given off from painted surfaces always affect guinea pigs more or less prejudicially. The fact that a guinea pig was unaffected by zinc white paint in the single experiment made by Breton can only be attributed to some accidental cause—guinea pigs, like painters, doubtless are not all equally sensitive to turpentine vapours.

Such then is the case against white lead. The French evidence that a minute amount of vapour containing lead is given off under the conditions of practice is not only unsubstantial but we have failed to corroborate it; and it is easy to see how the mistake arose. Prof. Baly's evidence, we venture to say, is rebutted by our observations; and he has himself admitted that he was in error in asserting that volatile compounds of lead are produced on heating white lead with linseed oil.

Prof. Baly, however, has introduced a new terror into painting in asserting that poisonous volatile organic substances are given off during drying—unsaturated aldehydes and so forth. But practice shows and all knowledge of the subject confirms this experience that this danger does not exist. Under the ordinary conditions of practice, such vapours are given off at such rate and in such quantity that their effect is negligible: only ultra-sensitive persons and those who are bent on being affected are likely to be disconcerted by them.

The production of such vapours is in no way confined to lead paints—as Prof. Baly recognises, they are the necessary outcome of the drying process. At most, it can be said, that they are produced most rapidly from white lead paint because this dries most rapidly—a circumstance which gives to white lead paint its special value.

It is clear that the real sinner in paint is turpentine; and any efficient substitute for turpentine that can be used will produce effects similar to those which this hydrocarbon produces, because the effects are those that are produced by volatile vapours generally.

Obviously, the only logical way to get over the vapour difficulty will be to abolish paints altogether.

After all, the real difficulty is the old one and on this point we need merely quote the closing sentences of the General Editor's Preface to the recently published authoritative work on Lead Poisoning and Lead Absorption by Dr. Legge, H.M. Medical Inspector of Factories, and Dr. Goadby:—

"The authors bring forward convincing evidence, experimental and statistical, in favour of the causation of lead poisoning by the inhalation of dust. This makes prevention a comparatively simple matter and the methods of prevention are effective and will contribute greatly to the health of the workers and the prevention of phthisis, which is so prevalent among lead-workers. Exhaust fans and hoods or vacuum cleaners, for carrying away the dust formed in the various processes—these are the simple means by which the dust can be removed and the workers' health assured."

In recent years, six European countries have made the use of lead paints the subject of exhaustive inquiry and the

*Comp. R. J. Carney, J. Amer. Chem. Soc., **34**, p. 32, and Chem. News, May 31, 1912

French alone have decided to prohibit their use. The law is due to take effect on January 1, 1915 but it is significant that it applies only to house painting and that its application is open to great latitude, being subject only to the ruling of a single Minister. There is doubt whether the law will be enforced. Thus the British Consul at Lille reported in August, 1912, as follows :—

"White lead.—There was no sensible modification in the white lead industry. The law prohibiting its use for outdoor painting purposes, which comes into operation three years hence, does not appear to be in favour with the public. For the use thereof has not decreased, whereas substitutes such as lithopone, etc., are being gradually left aside as consumers begin to discover their inferiority to white lead and it is doubtful whether the law will ever come into force."

From the history of the French enquiries, it appears that since 1786 French ministers have decreed on nine occasions that the use of white lead was to be discontinued, so far without any permanent result. It can scarcely be doubted that, as a rule, hygienic interests have been subordinated to polemics and it is important to note that the quantity of white lead used in France at the present time is greater than ever.

Regulations affecting the painting industry have been introduced in Austria, Belgium, Germany and Switzerland*; Holland has not yet taken action though inquiries have been held in that country.

In our own country, it is difficult to judge of the danger attending the use of white lead, as the Home Office returns are particularly weak regarding the incidence of disease and the death-rate among painters, as notification is not legally compulsory. Judging from the returns issued by the Registrar General, it would seem that the painter is in no way subject to any abnormal risk. It is beyond question that, in the past, symptoms have often been put down to lead poisoning which were in no way caused by lead and that the medical profession have much to learn in this respect. Now that the true sources of danger are understood, there should be no difficulty in reducing the risk to a minimum.

The properties of paints which are of practical consequence.—In conclusion, we venture to point out that these are broad issues to be discussed in connexion with the paint industry besides the question of possible toxicity, for is not the time at hand when those who are connected with its various branches will be called on to consider whether they will regulate or whether they will merely allow themselves to be regulated ?

We are advancing into an age when the "liberty of the subject" may become an unknown quantity; when sentiment and the opinion of an uninstructed majority will more and more prevail over sense and intelligence : unless these latter elements are organised not merely in their own defence but in the interest of the unintelligent majority. We need in this country to get rid of the prevailing belief in the ability of the so-called man of business to understand everybody's business besides his own and of his own absolute belief in himself; also we must be alive to the worse danger that is ahead of us, the calculating politician whose sole appeal will be to Demos. In some way or other, the belief in true expert knowledge, in the collective wisdom of men thoughtful and experienced, of knowing men, must be made to live among us and our proceedings must be ordered more upon their advice than is now the case. Some sense of our individual ignorance must come upon us all. Through ignorance, democracy has ruined many civilisations in the past : our one great chance of survival and improvement is to organise and apply science to neutralise ignorance ; if we cannot do that, our science will not avail us in the end.

It should be possible for a Society such as this to help in promoting the promulgation of a code of industrial ethics. The public will expect the introduction into the code of articles protecting them more than is the case at present against the use of unfit materials, against the bold and unblushing advertisement of rubbish.

The special question we would raise is whether it be not desirable to determine by collective action what are truly fit materials for painters' use—whether it be not to the interest of the trade to promote systematic inquiry which will make it possible to offer sound advice, if not to lay down rules for the general guidance. The Americans are already alive to this necessity and have conducted extensive inquiries with paints. There are very many problems awaiting solution.

The use of lead compounds in white paints.—Given the undoubted fact that lead can be so used that it need be no source of danger to the user, the question still remains—is it essential ? The verdict of experience is undoubtedly strong if not absolute in its favour, as is shown for example by the following quotation from the Report of the inquiry carried out by our Home Office twenty years ago :—

"In the past a large amount of thought, labour, time and money have been expended by many experts in the search for a substitute for carbonate of lead. Several compounds have been mentioned to the Committee as being equal to white lead and capable of taking its place, if only the prejudice of middle-men and dealers could be removed so as to secure for them a fair field in the paint market. One of these compounds and the one on which most stress has been laid is oxide of zinc. This has been used with success for internal decoration but for rough surfaces and for exposure to heat, cold and rain it does not possess the qualities for which white lead is conspicuous, namely, covering power and durability. Moreover, the price of oxide of zinc is greater than of carbonate of lead. With regard to all these so-called substitutes the Committee have invariably found that on closer inquiry of persons competent to judge and unprejudiced on either side, the substance in question was in some particulars inferior; and they have come to the conclusion that there is at present no substitute that can take the place of carbonate of lead."

In the interval, many improvements have been effected and the various substitutes are greatly superior in quality to those formerly offered. Nevertheless, at the present time, it cannot be maintained that any single pigment is suitable for all purposes and it is scarcely probable that such a pigment will ever be found. It is more probable that the solution of the problem will always lie in the proper selection of the pigment or pigments suitable for the particular purpose in view ; it has been clearly shown that the weakness of one pigment can be met by the addition of another or other pigments and that, in many cases, a mixture is advantageous.

The white pigments now in use in considerable quantity are only four—basic lead carbonate, basic lead sulphate, zinc oxide and the mixture of zinc sulphide and barium sulphate known as lithopone.

Basic lead sulphate.—This substance was introduced as a pigment by Bartlett in 1866—it has been used to a considerable extent in the United States of America during recent years. Lead sulphate has been proved to be a failure in practice. The oxy-sulphate apparently owes its value to the fact that, like white lead, it is a basic material. Being acted upon by acids, it is practically just as poisonous as white lead. Apparently it is less active than white lead towards drying oils but it is just as readily blackened by sulphuretted hydrogen.

Zinc white.—The use of zinc oxide as a pigment was first suggested by Courtois in 1780. It was introduced into commerce about 1846. Many improvements have been made in the methods of manufacturing it and in its quality,

* The following conclusions arrived at by a majority of the Swiss Commission are of interest :—

1. Le danger d'intoxication par les composés de plomb, employés dans les travaux du bâtiment, a Genève, est minime.
2. Il est possible, par des mesures de police, applicables aux chantiers, de diminuer encore, sinon d'éliminer complètement le nombre des cas de saturnisme professionnel parmi les ouvriers peintres en bâtiments.
3. Le remplacement de la céruse par l'oxyde de zinc mettrait l'industrie du bâtiment a Genève dans un état d'infériorité injustifiée.
4. L'oxyde de zinc n'a pas les qualités industrielles requises pour pouvoir remplacer avantageusement la céruse.
5. L'oxyde de zinc n'est pas si inoffensif qu'on veut bien le dire. En cherchant bien, on trouverait peut-être aussi quelques peccadilles à lui reprocher et pouvant motiver l'horreur que MM. les entrepreneurs en général et ceux de Genève en particulier éprouvent à son endroit.

La Ceruse, etc. Genève: W. Kündig et Fils. Rue du Vieux-College, 4. 1907.

the result being, that it now occupies a definite position as a pigment, but the statements that have been circulated of its superiority to white lead and in relative disparagement of this latter are not merely exaggerated but often false.

There are two types of zinc oxide on the market—the one known as "indirect" prepared by burning spelter; the other termed "direct" prepared from the ore. The latter usually but not always contains lead (as basic sulphate), owing to the presence of galena in the ore; when lead is present, this variety often has a bad colour owing to impurities other than lead contained in the ore. There is no generally accepted opinion as to the superiority of the one or the other type but it is claimed by the makers of the direct product that the presence of a small amount of lead increases the stability of the paint film. In view of the question we have raised as to the possibility of "lead" promoting the oxidation of the oil, this contention is well worth consideration. In Europe, the production of zinc oxide is practically limited to Belgium, owing to the monopoly this country has of zinc.

Lithopone.—This pigment is prepared by precipitating zinc sulphate with barium sulphide and is therefore a mixture of barium sulphate and zinc sulphide: but as it is subjected to furnace treatment to improve its physical condition it often contains some zinc oxide. One remarkable peculiarity of this pigment, which seriously affects its use, is the manner in which it changes in colour and darkens on exposure to light.

Ready-mixed paints.—The direct sale of ready-mixed paints is increasing in this country though the bulk of the white pigment sold is in the form of paste. In the United States of America ready mixed paints are purchased on a large scale by the painter. The paints sold are often composite, being mixtures of two or more of the following:—Zinc sulphide, white lead, zinc oxide, leaded zinc, lithopone, gypsum, talc, silica, alumina, barium carbonate, barytes (natural and artificial), calcium carbonate, magnesite, china clay, French chalk, asbestos. It has been found necessary in certain States of America to introduce legislation with regard to the labelling of such paints, requiring the chemical composition of the paint to be stated on every package so as to guard against fraud.

Value and suitability of paints.—The value of a paint is necessarily the outcome of a combination of more or less delicately balanced factors. The nature of the vehicle is of great importance and the fact that pigments other than the lead pigments require a larger proportion of oil is of fundamental significance in view of the well-known porosity of linseed oil films and of their tendency to shrink.

The case with which white lead may be applied is explained by the changes which take place between the oil and white lead. During the time of its storage as paste, chemical action takes place to a small extent and some lead is dissolved in the oil; this materially assists in the subsequent drying operations. In the case of zinc oxide or allied pigments, little or no change takes place, while the mixture is in the form of paste. When applied as a paint, in both cases the drying takes place by oxidation, although physically the two products differ considerably. In the case of lead paint, a film is obtained which has considerable elasticity, so that the contraction and expansion produced by variation of climatic conditions do not result in fracture of the film; whereas in the case of zinc paint, the oxidation product has a hard, brittle, inelastic surface, which does not change in unison with the surface on which the paint is applied. The ultimate product is hard and finally blisters and cracks or becomes translucent and peels off. The final result is a surface which is not so suitable for repainting as is that obtained when lead paint is used. We believe that for many purposes a mixture of white lead with zinc white is far superior to either singly.

The physical condition of a pigment must also be considered in relation to its powers of lasting. White lead is not a powder of uniform size, being invariably graded to some extent, as is apparent when the product is elutriated. This gives the film mechanical stability. The condition is imitated to some extent, in what are termed "reinforced paints," which consist of the previously named white lead substitutes ground together with asbestos or other inert materials of larger size, in order to imitate as closely as possible the condition naturally obtaining in white lead. White lead substitutes are invariably in an extremely fine state of division and regular in size; therefore, the reinforced effect cannot be obtained with these pigments alone. A practical result of this is the defect observed when the mouldings on doors are painted with the substitutes for white lead. It is quite useless to attempt to determine the painting value of any pigment on what might be termed straight painting: the intricacies afforded by mouldings and similar structures are the most conclusive test.

It is commonly objected that lead paints (both basic carbonate and sulphate) are blackened by sulphuretted hydrogen. But as a matter of fact, the blackening of paint out of doors is rarely due to this cause, being usually effected by smoke and dirt; convincing proof of this fact has been afforded of late years, since the process of cleansing by steam has been introduced.

The great cause of the decay of paints exposed out of doors appears to be the sulphurous and sulphuric acid in the atmosphere, especially in towns. It is stated that no less than 150,000 tons of sulphur are projected annually into the air of London, forming eventually some 600,000 tons of sulphuric acid.

Lead paints are scarcely affected by sulphurous and sulphuric acids, which if they act at all serve only to convert the oxide in the basic material into insoluble sulphate; but zinc paints (zinc white and lithopone) are most seriously affected by the conversion of the zinc oxide or sulphide into zinc sulphate—a substance easily soluble in water; the change is fatal to the painted surface. On this account, such paints are only suitable for use wherever rain has not access and should only be used in dry situations.

It is on points such as these we venture to think that the public and even painters need authoritative information: in the end, it must be to the interest of the trade as well as of the public that proper materials should be used and that the work done should be sound.

Conclusions. In conclusion we submit that it is clearly shown:—

1. That the vapours produced during the drying of white-lead pastes and paints do not contain lead.
2. That the vapours given off as paints dry consist of turpentine, for the most part, together with oxidation products of the oil and that these latter are common to paints generally containing oil so treated that it will dry.
3. That the oxidation products formed from the oil during drying are harmless under the conditions of practice, as has been shown by experiments with animals.
4. That the toxic effects sometimes experienced from drying paints are to be ascribed to turpentine and that due allowance must be made for this in dealing with the hygienic phase of the problem. Our inquiry also shows that in many cases effects have been regarded as due to "lead poisoning" which are attributable to other causes, especially to turpentine.
5. The whole available evidence indicates that the dangers attending the use of lead compounds are only the well-known mechanical dangers.
6. There is no foundation for the importation of a new element of danger into the consideration of the question of paints. Lead paints are to be objected to only on the ground that they may enter into the system through careless handling or in the form of dust such as is produced by rubbing down old paint.

Discussion.

Mr. Pearce, M.P., said that there appeared to be some fear lest there might be some legislative interference with white lead. Parliament acted carefully and with reluctance in those matters, and looked to the Departmental Committee for definite advice. If the question came seriously before the House of Commons, the paper would be of great advantage to the Members. He was sorry that Professor Baly was not present; he would like to have heard his views. They had no means of judging

Professor Baly's case; he was an authority on the subject. It was still more important from the House of Commons' point of view that the French Government had decided to prohibit the use of lead paint in 1915. If those two facts (although after the Paper he had heard they carried very little weight indeed, to his mind) had reached the House uncontradicted and unchallenged, they might have led to some legislative result, although even then he hardly thought so. At any rate Prof. Armstrong had rendered service by showing that white lead had been attacked unjustly. He was glad to know that a member of the Departmental Committee was present, and after what had been said and after the Report had been received and the Paper published he would be surprised if the House of Commons were ever called upon to take any action against white lead.

Mr. VICKERS said that for the last four or five years he had been periodically going to lectures on lead and zinc. One came away from one lecture feeling that zinc was the right and only thing, and from the next lecture that lead was the right and only thing. Manufacturers wanted to obtain durability. The question of inside painting presented little difficulty, but for outside work they always seemed to be faced with something. White lead always became chalky, with zinc there was hardness, and with lithophone there was no durability. A series of fences had been put up in America with the idea of applying to them paints made of all sorts of materials, and then having them watched. Two or three years ago the same suggestion was made to the Paint and Varnish Society, but nothing had been done. He would be very pleased to erect, and would give 150 guineas towards the cost of putting up, fences wherever the Paint and Varnish Society, the National Association of Master Painters, the Society of Chemical Industry, the Royal Institute of British Architects, the Society of Arts, or a combined Committee of them all, might desire, and let them supervise the fences and arrange what paints were to be put on them. As manufacturers, they wanted to know which was the most durable type of paint for outdoor work, and perhaps some small experiments might be made at the same time on iron work. If the Committee would accept the offer to continue for a test for three years or longer, he would be very pleased.

Mr. NOEL HEATON said that all technical men looked upon Baly's paper as of no real practical importance. Unfortunately, however, it was likely to have a very damaging effect amongst people who had no technical knowledge of the subject. On that account they must be grateful to Prof. Armstrong for so clearly putting before them the many weak points in his arguments. He hoped that those who had been trying to asperse the character of white lead would pay as much attention to Professor Armstrong as they had to Professor Baly. But from his point of view he did not think that the section of the paper dealing with the work of Baly was the most important part. To him the conclusions at the end of the paper were most valuable, and particularly the suggestions that were brought forward for the necessity of collective inquiry into the whole matter. During the past two years there had been far too much talk on this subject. An enormous amount of evidence had been collected by the Departmental Committee. But very little had been done in the way of getting at the bottom of the matter on scientific and practical lines. A practical investigation had been made in the United States, to ascertain whether they could do without white lead or what were the real facts about its use, and their results led inevitably to the conclusion to which Professor Armstrong had arrived, viz., that nothing could be substituted for it. Nevertheless they ought not to take their results at second hand, and should do something over here, as after all, the two climates were not the same. In common with a good many others he had been agitating for practical experiment on an organised scale for a considerable time, and he was indebted to Prof. Armstrong for putting forward the same proposition. From his own experience it was not possible to replace white lead by any substitute without loss of durability.

Mr. DAVIDSON said that Prof. Armstrong had well said that one must be very careful what deductions they made from the result of experiments. That it was proved conclusively that lead was not volatile in paints was of great service, and it was to be hoped that with the experiments suggested, they ought to be able to deal conclusively with the questions of efficiency and durability of the various paint pigments.

Mr. KIMBER referred to the tests carried out in America by H. A. Gardner, which indicated that zinc and zinc compounds behaved differently in different oil media.

Mr. ROWELL said that if white lead or manganese dioxide were mixed with linseed oil, a peculiar smell was produced. If that smell or emanation were poisonous, men who were daily boiling oil and varnish with oxidising agents such as manganese dioxide and lead oxide should be most subject to some sort of poisoning corresponding to Professor Baly's symptoms; but it was a fact that in varnish houses and oil boiling shops poisoning of that description did not occur, so that it might be said that emanations from paint, other than the turpentine smell, were not toxic in a marked degree.

A member said that he had had occasion to examine the deposit formed on the iron doors and ceilings in rooms where lead driers were used and on analysing he had found there was 10 per cent. of lead.

Mr. COSTE said that ordinary Russian turpentine was certainly very much more irritant and had very much more marked rubefacient properties than American turpentine. He had tried it by experiments.

Dr. MOLLWO PERKIN said that if Russian turpentine were properly purified it was not so; it was a splendid drier.

Professor ARMSTRONG, in reply, said he was very glad to hear of the willingness on the part of the trade to take up these matters and investigate them systematically; the results were likely to be of extreme value to the industry. Chalking was one of the great objections to white lead; on the other hand there was a difficulty with zinc paint, that it gave a very brittle film, and as had been pointed out, it was known that by combination of the two a very superior result was obtained. It ought to be possible by varying the medium and by working more in the direction of studying the effects produced by oils, something could be found which would get over the one real objection raised to white lead paint. There was no doubt that the medium played a very important part with zinc oxide, but the subject had been very inadequately studied. As regards the volatilisation of lead in the boiling house, he was certain if the speaker who made those remarks would look into the matter he would find there had been a mechanical transfer. It was very difficult to believe that anything like 10 per cent. of lead could ever be present through volatilisation.

He thought he might claim to have discovered Russian turpentine sometime in the seventies; he used then to examine all the turpentine that came into the Port of London to see whether it was contaminated with petroleum. In the paper he had pointed out that Russian turpentine produced effects which the American and French did not; especially were its physiological effects much more marked. What Dr. Perkin meant by properly purifying he did not know. By fractionation it was possible to get a product very similar to the French and American. Its peculiar effect was due to the presence of small quantities of products of heat and of destructive distillation. He believed that during manufacture it was customary to heat to a point very much beyond that which was customary in the case of the extraction of French and American oils. Of late years the smell which distinguished Russian turpentine had been got rid of by some method of treatment.

Mr. KLEIN wrote that in England no organised attempt had yet been made to determine the relative efficiency of the respective paint bases on scientific lines and until that was done little progress could be made in solving "the paint question." If it could be shown that the use of white lead constituted an abnormal source of danger to the user, and that at reasonable prices efficient substitutes were available then the case for prohibition might be considered to be on a sound footing. Recent work clearly showed that lead poisoning was readily amenable to regulations, and he had little doubt

that regulations of a reasonable type would effect a real improvement amongst house painters.

With reference to coach painting, he quoted the remarks of Dr. Collis (H.M. Medical Inspector of Factories) in the Annual Report of the Chief Inspector of Factories and Workshops, for the year 1910 (Cd. 5693, p. 175), dealing with coach painting, stating that he had visited three large railway works: "At the third works lead paint is used generally, but great care is exercised to prevent plumbism, no surface covered with lead is sandpapered, no burning off of lead paints is done, there is good lavatory accommodation and an excellent dining room and kitchen, where food brought by the men is cooked, are provided. The general health of the men is good." Such a statement left no question as to the efficiency of hygienic control in rendering coach painting a healthy occupation. At first sight prohibition would appear to be the simplest and most effective method of dealing with problems of industrial hygiene, but its logical application would prove the most effective barrier to progress yet devised, and its interference with chemical industries in particular would be intolerable.

Meeting held at Burlington House on Monday, March 3rd, 1913.

PROF. W. R. E. HODGKINSON IN THE CHAIR.

THE HEAT TEST. I.—GUNCOTTON. II.—NITROGLYCERIN AND CORDITE. III.—THEORETICAL.

BY ALFRED C. EGERTON.

Introductory.

The purpose of stability test is firstly to measure the extent of decomposition of an explosive, and secondly to gauge its liability to decompose. The latter is especially important when the test is used for accepting a new explosive, while both are important when the extent of deterioration of an old explosive is being determined. A stability test should be easy and quick to carry out and require an inexpensive apparatus. The test should be carried out under conditions similar to those to which it is normally exposed; it must not be affected by moisture and other volatile products in the explosive; lastly, it should be suitable for all explosives. In reviewing the many stability tests which have been devised, it cannot be said that any one of them satisfies all these conditions. A simple test is required which will satisfy these requirements and combine the good qualities of the Abel test, the Will test, and the Silver Vessel test; and which will be capable of differentiating between an impure and an unstable explosive, and which can be used either as an acceptance test or as a test of decomposition.

The present work started with an application to the amount of nitrogen oxides liberated during an Abel test, of a method of analysis of small quantities of gases by means of drops used as indicators. In the course of this analysis it was found necessary to investigate many features of the heat test not explainable from previous work. The work points to a method of carrying out the Abel test which might make it a thoroughly reliable and efficient stability test.

From the result of many observations the heat test has been found open to numerous errors. There is difficulty in securing absolute constancy in the reagents and in the paper employed; substances volatilising affect the reagent on the paper, and moisture causes dilution. Moreover the time taken for the test paper to be affected does not necessarily imply the rate at which the explosive will decompose, especially if small quantities of unstable substances are present; the assumption must be made with all due caution that these very slight decompositions mean that the explosive is so unstable as to give rise to dangerous decomposition on storage.

Robertson and Smart (this J., 1910, 130) have settled many points about the test, but there still remains much to be done, so some of their experiments were repeated and new ones devised to settle the more difficult points. The main points to be cleared up were:—

(1) What conditions affect the rate of decomposition of an explosive, and what substances are evolved from it?

(2) What is the source of the nitrogen oxides?

(3) Whether the indications of the test paper can be relied on?

(4) What is the relation connecting the concentration of NO_2 with time of colouring of reagent?

PART I.

Experiments with paper reagents.

To begin with, a large number of heat tests were made on samples of guncotton, the heat test tube and its contents were kept in the air out of the bath for an interval of 20 minutes between each test; tests were thus repeated on the same sample many times over. The experiments are set forth in detail in the complete paper.

The main results are, (a) that a test repeated a second time on guncotton is always lower than a first test; (b) that evacuation, which tends to draw out the products of decomposition, may either cause a rise or fall of the test depending on the condition of the guncotton and the circumstances of the test; (c) that the presence of moisture has a great deal to do with the time of the test.

A theory has been deduced from the experiments and it is probably a correct view of what occurs within the tube, since it is found to afford explanation for so many apparently discordant results. The reaction may be due to:—(1) The nitrogen oxides produced by a true decomposition of the guncotton during the test; (2) The nitrogen oxides from incompletely removed impurities; 3 The nitrogen peroxide dissolved in the guncotton. A proper stability test should distinguish between these three possibilities and measure the amount of nitric peroxide produced from each cause. Robertson and Smart describe experiments which show that normally prepared guncotton does not contain any appreciable quantity of peroxide in solution. The authors proceed to test the view that impurities give rise to the nitrogen peroxide produced during the test. They perform a continuous test on guncotton and find a fall in the test occurs, followed by a rise. The rise, according to them, does not indicate that the guncotton is getting more stable by the elimination of an impurity, but is simply due to the desiccation of the paper by the dried and heated guncotton, for when a trace of moisture is added the heat test again falls. The work here described shows that this is not the main cause of the rise in the test, though it agrees with the contention of Robertson and Smart that the heat test of a normal guncotton is not due to unremoved impurities. Robertson and Smart's view, then, of the heat test is that the nitrogen peroxide is produced by the decomposition of the explosive during the test, that any nitrogen peroxide in the tube is readily removable and that it is this peroxide which tends to lower the test on repetition, and that prolonged tests on dry guncotton are due to the desiccation of the paper. During this work, it was found, on the contrary that evacuation always lowers the test at first; if it was only the nitrogen peroxide left in the guncotton which tends to lower the test, evacuation must always increase it.

The idea of the actions in the tube gleaned from the work described in this paper is the following:—That on heating the guncotton nitrogen peroxide is evolved, some of the nitrogen peroxide is absorbed by the moisture in the guncotton, which latter also tends to vaporise and condense on the paper and on the walls of the tube, nitric and nitrous acids are thus formed in the guncotton, on the walls and on the paper. It is in the form of nitric acid that the guncotton absorbs "easily removable nitrogen peroxide"; not so much an absorption by the nitrocellulose itself as Robertson and Smart seem to imply in experiment (*loc. cit.* p. 132) of their paper, but an absorption of nitrogen