

THE CAUSE OF LEAD POISONING IN THE TINNING OF METALS.

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IN 1901 Miss Anderson (H.M. Principal Lady Inspector of Factories) and Dr Legge (H.M. Medical Inspector of Factories) were instructed by H.M. Chief Inspector of Factories to investigate the conditions of labour in the Tinning of metals and metal articles with a view to the preparation of regulations for the conduct of this industry. Difficulties having arisen in assigning a cause for the plumbism undoubtedly existing among workers, and preparation of regulations appearing impossible without some knowledge of the source of illness, the writer was instructed to assist them experimentally in determining the causes.

The results of the enquiry are contained in a report recently issued¹.

¹ *Tinning of Metals. Special report on dangerous or injurious processes in the coating of metal with lead or a mixture of lead and tin.* By Miss A. M. Anderson (H.M. Principal Lady Inspector of Factories) and T. M. Legge, M.D. (H.M. Medical Inspector of Factories). Together with a report on an experimental investigation into the conditions of work in tinning workshops by G. Elmhirst Duckering (one of H.M. Inspectors of Factories). Cd 3793. Price 1/-. Wyman and Sons, Ltd., Fetter Lane, E.C.

The present paper contains an account of the most important of the experiments carried out during the investigation and of their results.

Process and Trades affected.

The process of Tinning may be defined as "The coating of metal articles with lead or tin or a mixture of these metals." The objects aimed at are—(a) Protection of the metal from atmospheric influences, *i.e.* oxidation, corrosion, etc. (b) The rendering of vessels built up from component parts airtight and watertight. (c) Making subsequent operations of soldering more easy. (d) The joining together of loose parts. (e) The giving of a finished appearance to articles. Tinning for purposes described in *a, b, c* and *d* is of very real utility and there is strong evidence of extension of the process to various trades. It may be pointed out also that articles of iron or steel not previously tinned must be pickled, *i.e.* treated with acids, before soldering can be successful, whereas there is no necessity for pickling if they have been already tinned. This is of great importance where articles are produced by soldering together pieces which are made by separate operations.

In this paper only tinning with a mixture of lead and tin is dealt with and this has a wide application in the manufacture of—(1) Holloware including cooking utensils, kettles, iron drums, etc. (2) Harness furniture including the plating of harness, bits, buckles, etc. (3) Brass cocks and parts of gas and water fittings. (4) Cycles and motor cars, *i.e.* tinning of rims, radiators, etc. (5) Tin plates, *i.e.* the making of terne plates. (6) Boiler tubes.

The process of tinning is the same in principle in all cases though the details vary. The article, if made of iron or steel, is "pickled"—*i.e.* immersed in a bath of hot dilute hydrochloric or sulphuric acid until, by examination, it is found that all surface oxide is dissolved. If sulphuric acid is used it is then washed in water since presence of this acid or any of its salts prevents the adherence of the coating metals. After this washing, or immediately after pickling if hydrochloric acid is used, the article is immersed in a flux consisting of a solution of zinc chloride (frequently containing free hydrochloric acid) made by neutralising concentrated hydrochloric acid by means of metallic zinc. It is necessary to have a thin deposit of this flux on every part of the surface. It is then plunged below the surface of a molten mixture of lead and tin, containing from 35 per cent. to 90 per cent. of lead, held

in an iron vessel heated from below. Excess of metal is removed from the surface of the article, after taking it from the bath, while still in a molten state, by wiping with a pad of tow or shaking or by some equivalent operation. If the article is made of copper or brass or tin plate the preliminary cleaning by means of acid (pickling) is not necessary and it is at once dipped in flux and plunged into the molten metal.

Evidence of Lead poisoning.

Dr Legge has collected statistics relating to all cases of lead poisoning reported to the Factory Department during the eight years 1899 to 1906, as occurring in processes of tinning. These are given in the following tables¹.

TABLE I¹.

Showing the number of cases of lead poisoning reported in the two four-yearly periods 1899 to 1902 and 1903 to 1906 as occurring in tinning processes.

	1899 to 1902			1903 to 1906		
	Males	Females	Total	Males	Females	Total
Tinning of Holloware	15	14	29	13	22	35
Iron Drums and Kegs	11	—	11	24	—	24
Harness Furniture	8	—	8	7	—	7

This table he has supplemented by one showing the symptoms observed and the severity of the attacks, side by side with similar details relating to all the attacks of lead poisoning reported to the Factory Department during the years 1901 to 1904 inclusive, with the object of comparing the severity of the illness with that observed in lead industries taken as a whole.

In commenting on Table II Dr Legge says¹—

“In the tinning of holloware the severity of the attacks exceeds that noted in other tinning processes, and greatly exceeds that of the total lead poisoning cases for the years 1901 to 1904. The proportion of slight cases among men (10·7 per cent.) is without example in our experience in any lead industry. Third attacks or chronic plumbism among females engaged in the tinning of holloware is nearly five times as frequent as among females employed in lead industries as a whole. This is the more remarkable when the age of the women workers is borne in mind, the average age of the females attacked being only

¹ *Loc. cit.* p. 1.

18½ years as compared with 29 among a similar number of consecutive cases of plumbism in women in 1903."

TABLE II¹.

Showing details of all cases of lead poisoning reported in the eight years 1899 to 1906 as occurring in tinning processes, compared with similar details of all the cases reported as occurring in lead industries as a whole during the four years 1901 to 1904.

		Tinning of Holloware		Iron Drums and Kegs		Harness Furniture		Total		All Lead Industries 1901-1904	
		Attacks	Per cent.	Attacks	Per cent.	Attacks	Per cent.	Attacks	Per cent.	Attacks	Per cent.
Severity of Symptoms :											
Severe ...	{M	15	53·6	7	20·0	4	26·7	26	33·3	757	33·5
	{F	11	30·6	—	—	—	—	11	30·6	86	21·8
Moderate ...	{M	10	35·7	8	22·9	5	33·3	23	29·5	520	23·0
	{F	12	33·3	—	—	—	—	12	33·3	102	25·8
Light ...	{M	3	10·7	20	57·1	6	40·0	29	37·2	917	40·6
	{F	13	36·1	—	—	—	—	13	36·1	196	49·6
Not stated ...	{M	—	—	—	—	—	—	—	—	64	2·8
	{F	—	—	—	—	—	—	—	—	11	2·8
Number of Attack :											
First ...	{M	16	57·1	24	68·6	4	26·7	44	56·4	1451	64·3
	{F	16	44·4	—	—	—	—	16	44·4	300	75·9
Second ...	{M	8	28·6	5	14·3	4	26·7	17	21·8	348	15·4
	{F	12	33·3	—	—	—	—	12	33·3	62	15·7
Third ...	{M	4	14·3	3	8·6	7	46·7	14	17·9	361	16·0
	{F	8	22·2	—	—	—	—	8	22·2	18	4·6
Not stated ...	{M	—	—	3	8·6	—	—	3	3·9	98	4·3
	{F	—	—	—	—	—	—	—	—	15	3·8
Kind of Symptoms :											
Gastric ...	{M	22	78·6	29	82·9	9	60·0	60	76·9	1845	80·8
	{F	35	97·2	—	—	—	—	35	97·2	317	80·3
Narcotic ...	{M	12	42·9	7	20·0	6	40·0	25	32·1	479	21·2
	{F	7	16·6	—	—	—	—	7	19·4	61	15·4
Encephalopathic	{M	1	3·6	1	2·9	—	—	2	2·6	88	3·9
	{F	1	2·8	—	—	—	—	1	2·8	25	6·5
Rheumatic ...	{M	5	17·9	3	8·6	—	—	8	10·3	241	10·7
	{F	1	2·8	—	—	—	—	1	2·8	48	12·2

Dr Legge also examined a number of workers in tinning processes in 1901 and in 1906 and he gives the results in the following table, in which he also includes, for purposes of comparison, the results of examination of workers in other lead industries.

¹ *Loc. cit.* p. 1.

TABLE III¹.

Showing results of medical examination of workers in tinning and other lead processes. All the workers in tinning processes in sixteen factories were examined.

Occupation	Number examined		Blue Line			Anæmia			Wrist weakness					
	M	F	M	Per cent.	F	Per cent.	M	Per cent.	F	Per cent.	M	Per cent.	F	Per cent.
Tinning processes :														
Holloware (Tinner) 1906...	28	26	13	46.4	19	73.0	6	21.4	8	30.8	4	14.3	4	15.4
Holloware (Tinner) 1901...	43	25	18	41.9	13	52.0	15	34.9	8	32.0	4	9.3	1	4.0
Harness Furniture ...	25	—	13	52.0	—	—	14	56.0	—	—	4	16.0	—	—
Metal drums & casks (Tinners)...	20	—	14	70.0	—	—	8	40.0	—	—	3	15.0	—	—
Total tinner in holloware, harness furniture & metal casks (1901) ...	98	—	45	45.9	—	—	37	37.8	—	—	11	11.2	—	—
Enamelling processes :														
Baths ...	83	—	40	48.2	—	—	25	30.1	—	—	7	8.4	—	—
Copper letters, etc. ...	12	103	3	—	43	41.8	1	—	45	43.7	—	—	5	4.8
Sheet iron—														
(1) With use of lead														
Factory 1 ...	2	41	1	—	18	43.9	1	—	19	46.3	—	—	1	2.4
Factory 2 ...	11	44	4	—	16	36.3	1	—	10	22.5	—	—	—	—
(2) Without use of lead...														
Jewellery & watch dials ...	44	31	4	9.1	6	19.4	2	4.5	4	12.9	—	—	—	—
Yarn dyeing with chromate of lead ...	45	139	9	20.0	20	14.4	2	4.4	22	15.8	—	—	1	0.7
Paints & colours ...	251	—	103	41.0	—	—	88	35.0	—	—	9	3.6	—	—

In the particular factory where the experiments were carried out one case of lead poisoning was reported in 1903 in which the symptoms were recorded as long standing paralysis, and a second in which they were colic, headache, dimness of vision, and general weakness. The former patient died a few months later from pulmonary tuberculosis. Dr Legge examined the three men at work during the experiments. Two of them doing the greater part of the common tinning were markedly anæmic and had a blue line, and the third, who was only irregularly at work in the tinning workshop and then chiefly at bright tinning (pure tin), showed a trace of a blue line only. One of the former was reported as suffering from lead poisoning early in 1907.

¹ *Loc. cit.* p. 1.

Preliminary investigation.

It appeared possible from a preliminary examination of the process of tinning as carried on in works where cases of lead poisoning had occurred that the illness might be caused by—(a) Inhalation of vapour of lead chloride, produced by interaction of the hydrochloric acid and zinc chloride necessarily present on the surface of the article to be tinned at the moment it is brought in contact with the molten metal, with the lead of the tinning mixture, and vapourised at the temperature of the molten metal. (b) By inhalation of minute particles of metal or lead chloride in the solid state caused to enter the air by the mechanical action of the rapidly escaping vapour produced below the surface of the molten metal when the article to be tinned is thrust into the metal bath. (c) By inhalation of dust containing lead or compounds of lead caused to float in the air by sweeping the sides of the bath, etc. (d) By want of cleanliness on the part of workers. A number of experiments in which air was aspirated from a point over the molten metal during tinning, and bubbled through water, were carried out, and the washing liquid subsequently examined qualitatively. In all cases minute quantities of lead were found to be present in the form of chloride. Zinc chloride and free hydrochloric acid were also invariably found and in some cases a compound of tin was present. The washing liquid remained quite clear except in one case where the experiment was of a more lengthy nature. In this a white precipitate formed and proved to be pure oxide of tin. The lead was always found in solution.

Large deposits of dust were invariably observed on every ledge in tinning workshops, and samples of this were taken from various points and qualitatively examined. Those samples taken from points near a tinning bath contained considerable quantities of lead chloride and also some lead insoluble in water. Zinc chloride, copper chloride and a compound of tin were also observed. Samples collected from points remote from a tinning bath appeared to contain small quantities only of lead chloride, but lead insoluble in water was always noted. Large quantities of fibre apparently similar to the tow used in wiping excess of metal from the tinned article were invariably observed in the samples of dust from whatever point collected. It therefore appeared that the dissemination of particles of fibre carrying small quantities of lead and lead chloride, rubbed off the hot tinned surface during wiping, might be a further source of lead poisoning. As a result of this preliminary investigation more accurate experiments were devised with

a view to showing the extent and source of contamination of the atmosphere by compounds of lead, etc.

Accuracy of experiments and results.

The difficulties in the way of arriving at any accurate knowledge of the quantities of foreign substances present in the atmosphere of a tinning workshop were immense. The preliminary investigation indicated that the actual amounts of any deleterious substance present at any given time are not only small, but also that they vary enormously in different parts of the workshop and also in the same position at different times according to the nature of the work being carried on. It appeared hopeless to attempt to obtain accurate results by means of analyses of air, and moreover from the point of view of the enquiry such results would have very little value since on account of the variations in the state of the atmosphere they could not be applied with any certainty to show the probable effect on the health of the workers. The most promising line of investigation appeared to be to ascertain the quantities of various deleterious substances present in a large volume of air taken continuously from a given point during a considerable period of time, and to compare the results with the average time spent and the average amounts of air inhaled by a worker at a particular operation—in other words to ascertain what quantities of deleterious substances a worker would on the average inhale in a given time. Under such conditions there appeared to be no possibility of dealing with scientifically accurate volumes of air reduced to normal temperature and pressure, since not only were the volumes to be examined very large in the total but it was necessary to carry on some of the experiments from day to day for several days, during which the temperature and pressure would vary continuously. Hence it is not claimed that the experiments and their results show accurately the composition of the air of a tinning workshop at a given time. It is however claimed that they show the approximate amounts of deleterious substances inhaled by workers during given periods of time, and that they may be used as a basis for calculation of the effects on their health when exposed to such conditions as obtain in tinning workshops.

Quantities of deleterious substances inhaled by workers.

This section is inserted here for convenience, but the quantities of deleterious substances inhaled by workers are calculated from experimental data which are given in subsequent sections dealing with the experiments. The substances experimentally found to exist in the atmosphere of a tinning workshop consist of hydrochloric acid and chlorides of lead, zinc, iron and copper in the state of vapour, or closely approaching that state, with metallic tin and lead carried mechanically on fibre from the tow used in wiping. Hydrochloric acid is however only observed in quantity in the immediate neighbourhood of the baths though it probably collects also near the roof. The quantity of any of these substances present in the air at a given time is very small. Thus it would appear that, in the neighbourhood of the tinning baths and wiping stands, the quantity of lead chloride ranges from approximately two parts to sixty parts per ten million parts by weight of air. Dr Legge however points out in quoting medical authorities that it is not so much the quantity of lead taken in any case which determines the symptoms as its continued introduction, and also that for the production of chronic plumbism long continued absorption of small quantities of lead is necessary¹. The effect on the health of workers of long continued absorption of small quantities of such compounds as hydrochloric acid and chlorides of zinc, tin, copper and iron must be left to medical authorities, but apparently it must at least result in impaired vitality. In the following table an attempt (based on the experimental data subsequently given) has been made to estimate the quantities of various deleterious substances inhaled by workers per day and per year. The method of arriving at the results given was as follows: the actual average time a tinner, who prepares his own work, spends in the tinning workshop during tinning and wiping, as distinguished from the time spent outside in preparing his work (*i.e.* pickling, etc.), was ascertained by observation extending over several weeks. It worked out at slightly over $5\frac{1}{2}$ hours per day. Taking the average quantity of air inhaled by a man as 18 cubic feet per hour, a day's work would involve his breathing about 100 cubic feet of the air of the tinning workshop during the times when fumes are being produced. The same data are available whether a worker does tinning or wiping since these operations are interdependent. Hence it is possible to calculate the results shown in the table.

¹ *Loc. cit.* p. 1.

TABLE IV.

Showing the quantities of deleterious substances inhaled by workers in a tinning workshop.

The following assumptions are made:

- Average volume of air inhaled at each inspiration = 30.5 cubic inches¹.
 Average number of inspirations per minute = 17¹.
 Average time spent in tinning, wiping, etc. per day = 5 hours, 34 minutes.
 Average number of days worked per week = 5.
 Average number of weeks worked per year = 50 weeks = 250 days.

N.B. The figures in brackets are the quantities of the various compounds expressed in grams.

Worker affected	Distinctive no. of exp. on which conclusion is based	Quantities expressed in grams of deleterious substances inhaled by workers in a tinning workshop per day and per year								
		Soluble in water					Insoluble in water			
		Chlorides of				Hydrochloric acid	Oxide of tin	Metallic		
		Lead	Zinc	Iron	Copper			Tin	Lead	
Tinner using open tinning bath	Per day	5	0.0143 (0.221)	0.0607 (0.937)	0.0250 (0.386)	Trace	0.3897 (6.014)	0.0070 (0.011)	—	—
	Per year	5	3.575 (55.169)	15.175 (234.181)	6.250 (96.45)	Small amt. (1503.463)	97.425	1.750 (27.006)	—	—
Tinner using bath covered by hood & having fumes exhausted by draught offurnacechimney	Per day	6	0.0024 (0.037)	0.0155 (0.239)	0.0052 (0.080)	Trace	0.0090 (0.014)	0.0018 (0.028)	—	—
	Per year	6	0.600 (9.259)	3.875 (59.799)	1.300 (20.062)	Small amt.	2.250 (34.722)	0.450 (6.944)	—	—
Tinner using open bath and wearing respirator	Per day	7	0.0034 (0.052)	0.0075 (0.116)	0.0069 (0.106)	—	0.2879 (4.443)	Trace	—	—
	Per year	7	0.850 (13.117)	1.875 (28.935)	1.725 (26.620)	—	71.975 (1110.718)	Small amt.	—	—
Wiper	Per day	8	0.0191 (0.294)	0.0125 (0.193)	0.0091 (0.222)	—	Nil	0.0068 (0.105)	0.0259 (0.400)	0.0211 (0.326)
	Per year	8	4.775 (73.688)	3.125 (48.125)	2.275 (35.108)	—	Nil	1.700 (26.234)	6.475 (99.922)	5.275 (81.404)

For reasons stated in subsequent sections the quantities of deleterious substances given in the table as being inhaled by workers at an open bath, with or without a respirator, must be taken as the minimum. Actually they would probably inhale somewhat larger quantities. Consideration of this table shows that of all the persons working in a tinning workshop those doing wiping are exposed to most

¹ *Hygiene and Public Health*, by Parkes and Kenwood, p. 211.

danger from lead chloride in the form of vapour, or in a state closely approaching that of vapour, though a tinner using an open bath (which is not very general) would be exposed to almost as much risk. The results are exceedingly interesting and fully support Dr Legge and the medical authorities he quotes in the statement that long continued absorption of small quantities of lead is a factor of much more importance in causing lead poisoning than the amount of the dose. There can be no doubt, as will be seen later, that vapour of lead chloride is being continually given off from the tinned article for some time after its removal from the bath, probably in decreasing quantity till the coating is set and hard.

Experimental.

The whole of the laborious quantitative analyses were carried out by Dr Thorpe, C.B., F.R.S., in the Government Laboratory, and we desire to take this opportunity of publicly acknowledging our indebtedness to him and to Mr E. Grant Hooper, also of the Government Laboratory, for their able assistance in this respect.

The investigation naturally divided itself into three parts—(a) A series of laboratory experiments under conditions allowing of control of any fumes produced. (b) A series of workshop experiments. (c) The collection of samples of dust from selected points and their subsequent examination in order to obtain some knowledge of the distribution of the deleterious substances in the atmosphere.

After a large number of preliminary experiments the following general method of examination of the atmosphere was adopted. An aspirator consisting of an ordinary filter pump attached to a water tap was connected by red rubber pressure tubing to the outlet pipe of a measuring instrument. This was a specially made wet gas meter, of the type used in research work on coal gas, designed to accurately measure volumes of gas, but suitably altered for these experiments. It was fitted with devices for maintaining the water at the same level as that of calibration and also with a glass observation chamber in which was fitted a thermometer. The inlet pipe of this instrument was connected by pressure tubing to an absorption apparatus consisting of two tall glass vessels each containing about 180 c.c. of distilled water and connected with each other in such a way that, on allowing water to pass through the aspirator, air was bubbled through the water in each vessel in succession and was then passed through the meter in order to

measure its volume. In most cases it was found that the absorption apparatus acted as a very efficient filter, the air being freed from all foreign substances during passage through it. In order to ensure its isolation and to prevent accidental introduction of impurities large glass bulbs were fitted to the inlet tube of one and the outlet tube of the other vessel of the absorption apparatus. To the inlet bulb was attached a gun metal funnel inside of which were fitted two removable iron gauze diaphragms three inches apart, in order to further ensure isolation of the absorption apparatus and to prevent small splashes of metal finding their way into it. In some experiments the space between the diaphragms was filled with closely packed glass wool, the object of its insertion being to differentiate between fumes and dust, the preliminary experiments having shown that while this material effectively filtered dust from the air it was not capable of entirely preventing passage of vapour. In the workshop experiments the whole of the absorption apparatus was clamped to a retort stand and it could thus be placed with the mouth of the funnel at any point from which it was desired to aspirate air, the rubber tubing connecting it with the meter having a length of about forty feet. The air from the selected point was thus passed through the gauze diaphragms and glass wool filter in the funnel, through the inlet guard bulb and then through the water in each vessel in turn. The foreign substances remained either in the glass wool or in the water filters while the air passed on to the meter. The object of having a second washing vessel was so that it might act as a control on the first and afford some guide as to whether filtration was efficient. The apparatus was watched during the whole time of experiment and observations of temperature and volume aspirated were made every fifteen minutes.

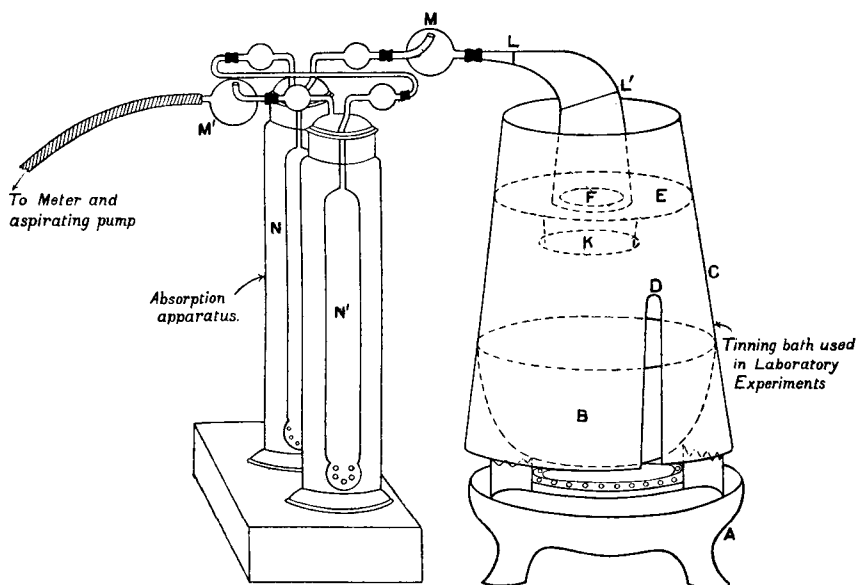
Sketch of apparatus used.

The absorption apparatus is shown on the left and the tinning bath used in the laboratory experiments on the right. The sketch shows the apparatus as fitted up for the laboratory experiments.

Laboratory experiments.

In these experiments it was necessary to have any fumes produced under control while reproducing as far as possible the conditions of tinning. After many attempts, which showed considerable danger of injury from explosions in the molten metal, the following method was

devised. A thin iron bowl capable of holding about 1200 grams of molten metal was supported on a Fletcher gas burner and completely covered by an iron cowl in the form of a frustum of a cone having at one side a vertical slot about $\frac{3}{4}$ in. wide extending about $2\frac{1}{2}$ ins. above the edge of the bowl. Inside the cowl and about $3\frac{1}{2}$ ins. above the surface of the molten metal an iron disc was fitted, having at its centre a circular orifice slightly smaller than the mouth of the funnel of



- A. A gas burner for heating B which is a thin iron bowl, capable of holding about 1200 grams of molten tinning metal, resting on supports on the burner A.
- C. An iron cowl fitting closely over B and having a slot D about $\frac{3}{4}$ in. wide cut in it to admit of introduction of articles to be tinned.
- E. A disc of iron, fastened inside C, having a circular hole F cut at its centre and a second disc K attached to it below and slightly larger than the hole F. Its object was, while allowing of passage of fumes, to prevent molten metal from splashing upwards.
- LL'. A gun metal funnel forming part of, and attached by rubber tubing to, the absorption apparatus. In an experiment the absorption apparatus was so placed as to bring the mouth of the funnel to the point from which it was desired to aspirate air. Thus in the illustration it is shown fitted over the hole F in the disc E above the tinning bath used in the laboratory experiments. At L and L' iron gauze diaphragms were fastened inside the funnel and the space of 3 inches between them was in some experiments filled with closely packed glass wool.
- M and M'. Large glass guard bulbs attached by rubber tubing to the inlet and outlet tubes respectively of the washing vessels.
- N and N'. First and second washing vessel respectively, each containing about 180 c.c. of distilled water.

the absorption apparatus, and about an inch below this another iron disc was suspended, larger than the orifice but not so large as the first disc, but completely preventing direct splashing of metal through the orifice. The funnel of the absorption apparatus was fixed in contact with the upper disc so as to completely cover the orifice. The object of the discs as arranged was to confine the atmosphere above the molten metal and allow its passage into the absorption apparatus while preventing splashing of metal into the funnel.

Experiments I and II. The objects of the first two experiments were (a) To show the effect of the violent escape of vapour, produced below the surface of molten metal, in causing contamination of air, (b) To ascertain the nature of these contaminating substances, and (c) To ascertain whether they can be filtered from air by a material capable of use in a respirator. As the effect of violently escaping vapour on molten metal is, from one point of view at least, purely mechanical, it was necessary in these experiments to avoid any complicating chemical action. Hence no hydrochloric acid or zinc chloride flux could be used. At the same time it was necessary to reproduce the process of tinning as performed in a workshop as far as possible. A tinning metal consisting of a mixture of half lead and half tin was made by weighing out the pure metals separately, melting them together and removing all dross. The metal was then placed in the iron bowl described, and the apparatus fitted up. A number of pieces of iron about one inch square were bent so as to afford a holding surface for liquid and each of these was held in a pair of slender crucible tongs, dipped in distilled water and immediately introduced through the slot in the cowl covering the bowl and plunged into the molten metal. Aspiration was commenced after the introduction of the third piece of iron and was continued at the rate of about four cubic feet per hour. The rate at which the wet pieces of iron were introduced was about eighty per hour. Alarming and violent explosions occurred as they came in contact with the molten metal and it was at once noted that these were much more intense than anything which occurs in actual tinning. It was quickly apparent that contamination of the atmosphere can be caused in this way since a grey sediment began to collect in the absorption apparatus. The space between the gauze diaphragms was not, in the first experiment, filled with glass wool and at the close of this experiment a considerable deposit of a heavy extremely finely divided greyish black powder was found in both the inlet guard bulb and in the first washing vessel but not in the second. A deposit of the

same dust was noted on surfaces near the apparatus and on the surface of the molten metal. The contents of the inlet guard bulb and the first washing vessel were examined separately. In the former the substance deposited was found to consist principally of metallic tin and lead oxide with a smaller proportion of tin oxide. In the washing vessel the substance deposited was found to consist of tin oxide, metallic tin, and lead oxide in nearly equal proportions. In both samples the ratio of tin to lead was much greater than in the metal from which they were derived, showing that the tin is more readily caused to enter the atmosphere than lead.

In the second experiment the space of three inches between the gauze diaphragms in the funnel of the absorption apparatus was filled with closely packed glass wool, but in other respects the method followed was exactly the same as in Exp. I. Cotton wool would no doubt have been a better filtering material than glass wool but preliminary experiments had shown that the fumes produced in tinning quickly condensed in cotton wool and prevented passage of air, and, since it was desired to make the experiments comparable as far as possible, glass wool was therefore used in all those experiments where an additional filter was required. The phenomena noted were similar to those observed in the first experiment with the significant exception that no deposit of dust could be observed in either the guard bulb or the washing vessel, though the volume of air aspirated was more than double and the length of the experiment twice that of the first experiment. At the end the glass wool composing the lower eighth of an inch of the filter was found to contain a considerable quantity of the finely divided greyish black powder and for a space of half an inch the filter was slightly discoloured. The remainder was however quite clean and bright indicating that efficient filtration of dust from the air had been obtained. The liquid condensed in the inlet guard bulb and the contents of the first washing vessel were washed into one sample bottle and examined together. The analytical report however stated that no lead, tin or other solid substance was present. It was in fact still pure distilled water. The analysis of the black powder collected in the glass wool filter showed it to be of the same approximate composition as that of the two samples, collected in the first experiment, combined. The results of the two experiments are summarised in the following table.

The results of the two experiments clearly show that the mechanical action of escaping vapour produced below the surface of molten metal may be a serious factor in causing contamination of the atmosphere by

TABLE V.

Showing the quantities of deleterious substances collected in the absorption apparatus in experiments showing the effect of the mechanical action of escaping vapour, produced below the surface of molten metal, in causing contamination of the air.

The percentage composition of the foreign matters present in the air is shown by the figures in brackets below those expressing the quantities. In Experiment I the figures given are the combined results of examination of two samples collected separately. In Experiment II the percentage composition is stated as the result of examination of dust collected in the glass wool filter.

Exp. in which collected	Volume in cubic feet aspirated	Quantities expressed in grams of various deleterious substances found deposited in washing vessels								Ratio $\frac{\text{Tin}}{\text{Lead}}$	
		In solution			In suspension					In sample	In original tinning mixture
		Calculated as metal		Sulphuric acid	Metallic tin	Tin oxide	Metallic lead	Lead oxide	Iron oxide		
		Lead	Tin								
I	10-0000	0-0014 (0-28)	0-0111 (2-24)	Trace (Trace)	0-2066 (41-64)	0-0725 (14-61)	Nil (Nil)	0-2008 (40-48)	0-0037 (0-75)	$\frac{1-46}{1}$	$\frac{1}{1}$
II	20-0117	Nil —	Nil —	Nil —	Nil (45-30)	Nil (14-20)	Nil (Nil)	Nil (39-90)	Nil (0-60)	$\frac{1-5}{1}$	$\frac{1}{1}$

lead and tin either in the form of dust or fume or both, the lead being in the form of oxide and the tin in the form of both metal and oxide. They also show that whatever the origin of the contaminating substances whether as dust or fume or spray their inhalation can be readily prevented by use of a respirator. A further conclusion and one of great importance in following experiments is that glass wool arranged in the manner described is perfectly efficient as a filter for removing dust from the air drawn through it.

Experiments III and IV. These experiments were devised to afford information as to (a) The nature of the emanations from the tinning bath, (b) Whether the deleterious substances exist in the air as vapour or dust and as to the possibility of filtering them from the air by material capable of use in a respirator. The apparatus used and the general method followed were the same as in the first two experiments but the processes of tinning were exactly reproduced. A solution of zinc chloride was prepared by adding excess of zinc to pure concentrated hydrochloric acid and the pieces of iron were immersed in warm dilute hydrochloric acid till free from all surface oxide. They were then drained free of excess of acid, dipped singly in the zinc chloride solution (flux) and introduced into the molten metal through the slot in the cowl

over the metal bath, the rate of tinning being about 60 pieces per hour. On removal from the molten metal they were found to be properly tinned. In Exp. III the space between the gauze diaphragms of the funnel of the absorption apparatus was empty but in Exp. IV this was filled with closely packed glass wool. In both experiments immediately on commencing tinning and aspiration the whole apparatus became filled with dense white fumes, and in about fifteen or twenty minutes a faint milkiness was observed in the liquids of the washing vessels and this gradually increased till a considerable quantity of a creamy white precipitate was produced in each vessel, though that in the first was greater in quantity than in the second. Exp. IV had to be interrupted several times and the apparatus dismantled in order to renew the glass wool filter, the condensation of fumes in it causing complete cessation of passage of air. In no other respect was any outward difference to be observed in the phenomena noted in the two experiments. On ceasing aspiration a bluish vapour was observed issuing from the slot in the cowl and aspiration was therefore continued for some time after tinning had ceased, but in Exp. IV blocking of the glass wool filter was then very rapid, the lower part becoming completely cemented up by a white highly deliquescent substance. No dust was observed as in the first pair of experiments, but at the conclusion of each experiment it was noted that a yellowish grey soft pasty semi-fused mass of some substance had collected on the surface of the molten metal (this is to be observed also in workshop tinning baths) which, on cooling, solidified into a hard greyish resinous looking substance. The blue vapour was seen to rise from it when hot. On the inside of the cowl and funnel there was a deposit of a white intensely deliquescent substance and round the gauze diaphragms and the lower edges of the funnel there were fringes of white needle shaped crystals which were not deliquescent. All these phenomena appear to point to the production of true vapour during tinning. The contents of each washing vessel were examined separately and it was found in both experiments in each case that the condensed fumes consisted of lead chloride, zinc chloride, iron chloride and hydrochloric acid in solution while the creamy white precipitate was oxide of tin. In Exp. IV the amount of lead chloride was about two-thirds, that of zinc chloride five-sixths, that of hydrochloric acid about double and that of tin oxide about one-third more than that found in the absorption apparatus in Exp. III, though the air in the former case had to pass through three inches of closely packed glass wool before reaching the washing vessels, while its passage was quite uninterrupted

in the latter case. No examination was made of the glass wool filter. A striking difference was observed in the behaviour of the molten metal when the pieces of iron previously dipped in zinc chloride flux were plunged below its surface as compared with the same operation with pieces of iron previously dipped in water. In the latter case explosions, always violent and frequently alarmingly so, occurred, while in the former there was a mild bubbling only of the metal. Hence though the mechanical action of escaping vapour in causing contamination of the atmosphere cannot be ignored it is to be concluded that the effect in actual tinning is not nearly so pronounced as might be expected from the results of Exps. I and II. The pasty substance collecting on the surface of the molten metal must also tend to prevent the production of dust. It is striking that while in Exp. II it was conclusively shown that all the substances caused to enter the air by the purely mechanical action of escaping vapour could quite easily be filtered from the air by means of a mechanical filter, Exp. IV shows that the substances caused to contaminate the atmosphere in actual tinning cannot be separated in this way. It is noteworthy also that tin oxide should be found in solid form in the washing vessels in Exp. IV. It could not pass the glass wool filter in this state and it is equally impossible that it could exist in the air as vapour of tin oxide. One is therefore driven to the conclusion that it must be caused to enter the atmosphere as the vapour of some compound of tin capable of decomposition by water—probably as tin chloride. The results of Exps. III and IV are given in the following table.

The conclusions drawn from the two experiments are—(a) That the processes of tinning cause the atmosphere to become impregnated with hydrochloric acid and chlorides of lead, zinc, iron and probably tin. (b) Use of a respirator by workers is impossible by reason of the tendency of the chlorides to condense and block up the filtering material. (c) Even if possible of use inhalation of substances caused to contaminate the air by tinning cannot be prevented by use of a respirator. (d) The mechanical action of escaping vapour is not nearly so important a factor in causing air contamination as the chemical action of the materials (acid and flux) used in tinning on the tinning metal and subsequent vapourisation of the products of this action.

A comparison of the results of Experiment I with those of Experiments III and IV brings out a striking point. The experiments are strictly comparable, the only radical difference being that in I distilled water only and in III and IV hydrochloric acid and zinc chloride

TABLE VI.

Showing the quantities of deleterious substances condensed in the absorption apparatus after having been caused to enter the air by the process of tinning as conducted in laboratory Experiments III and IV.

The percentage composition of the foreign matters thus filtered from the atmosphere is shown by the figures in brackets given below those showing the quantities of the various deleterious substances.

Volume in cubic feet of air aspired	Quantities expressed in grams of deleterious substances condensed in absorption apparatus in each experiment									Ratio	
	In solution					In suspension				In samples	Tin Lead
	Chlorides of				Hydrochloric acid	Oxides of					
	Lead	Zinc	Iron	Copper		Tin	Lead	Iron	Zinc		
14·0000	0·0384 (3·37)	0·6620 (58·17)	0·0041 (0·36)	—	0·3240 (28·47)	0·1082 (9·51)	0·0010 (0·09)	0·0003 (0·02)	Trace	$\frac{2·9}{1}$	$\frac{1}{1}$
14·5800	0·0233 (1·52)	0·5530 (36·14)	0·0021 (0·14)	—	0·8150 (53·26)	0·1361 (8·89)	0·0006 (0·04)	0·0002 (0·01)	Trace	$\frac{5·99}{1}$	$\frac{1}{1}$

solution were brought into contact with molten metal. In Experiment I it is shown that 10 c. ft. of air contained 210·2 milligrams of lead oxide while in the third experiment 14·0 c. ft. are shown to contain only 38·4 milligrams of lead chloride and 1 milligram of lead oxide. Further it is shown by Experiment II that all the products of mechanical action of escaping vapour can be filtered from air by means of the glass wool filter, while in Experiment IV after passage through an exactly similar filter 14·58 c. ft. of air are shown to contain 23·3 milligrams of lead chloride and 0·6 milligram of lead oxide (very probably this is really lead chloride mechanically held entangled in the tin oxide precipitate). The difference in the amounts of lead chloride in the air shown by Experiments III and IV, *i.e.* 15·1 milligrams, must be ascribed to the use of the glass wool filter, and any substances caused to enter the air in these experiments by the mechanical action of escaping vapour would certainly be arrested by it. Hence the quantity of lead oxide caused to contaminate the air in this way must be considerably less than 15·1 milligrams, since there can be no reasonable doubt that some of the lead chloride vapour also condensed in the filter and therefore formed part of the difference of 15·1 milligrams shown. The result shows that the mechanical action of vapour in producing air contamination in tinning is small as compared with that of chemical action.

¹ In this experiment the air before passing through the liquid in the absorption apparatus was drawn through 3 inches of closely packed glass wool.

Workshop experiments.

In the workshop experiments the method of examination of the air was exactly the same as that described in Experiments I to IV, the absorption apparatus being placed in such a position as to bring the mouth of the funnel to the point from which it was desired to aspirate air.

Experiment V. The object of this experiment was—(a) To obtain information as to the amount and nature of the contamination of air caused by actual tinning, *i.e.* dipping. (b) To afford a basis for calculation of the danger to and effect on the health of a tinner using an open bath. It was carried out in connection with a tinning bath provided with a hood completely enclosing the metal bath on three sides and provided with exhaust as good as it is possible to obtain by means of an opening from the hood into the furnace chimney. The day was bright and sunny and fumes were removed fairly quickly, the atmosphere being free from the choking property usually associated with tinning workshops. The metal was new and was bright and clean and aspiration was continued for some time when no tinning was in progress. It is to be expected therefore that the results are lower than would on the average be obtained if the tinning bath were quite open, and that they show the minimum danger to which a tinner using an open bath would be exposed. The space between the gauze diaphragms in the funnel of the absorption apparatus was not filled with glass wool and the air over the molten metal was therefore drawn directly through the distilled water in the washing vessels after passage only through the two gauze diaphragms and the guard bulb. The absorption apparatus was placed in such a position inside the hood over the tinning bath as to bring the mouth of the funnel nearly over the centre of and about ten inches above the molten metal. The contents of each washing vessel were separately examined and the results of analysis showed the atmosphere over the bath to be impregnated with hydrochloric acid and chlorides of lead, tin, zinc and iron, and that a tinner using an open bath must inhale considerable quantities of these substances.

Experiment VI. This experiment was devised for the purpose of showing—(a) The condition of the atmosphere at a moderate distance from the metal bath. (b) The danger to the health of a tinner working at a bath provided with a hood and exhaust by connection with the furnace chimney. It was carried out in connection with the same bath as Experiment V, but the days were less favourable to the

escape of fumes and the atmosphere during parts of the experiment was bad. The hood completely enclosed the bath except at the front where the tinner works and this was partly closed by an iron apron suspended from the top of the hood. The absorption apparatus was suspended in such a position as to bring the mouth of the funnel exactly on a level with the tinner's nose (indeed he had to exercise care to avoid knocking it) and about eight inches outside and away from the apron partly closing the front of the hood, and about one foot above its lower edge. In this way only the air actually possible of inhalation by the worker was drawn through the apparatus and direct access of fumes from the molten metal bath was impossible. Blue vapours could occasionally be seen rising from the articles as they were removed from the tinning bath to the wiping stand and also issuing from below the lower edge of the apron covering part of the front of the hood. The experiment was continued from day to day till 100 c. ft. of air had passed through the absorption apparatus and occupied five days in all. It had previously been noted that fumes containing lead chloride became deposited on the outside of the apparatus and in all the experiments great care was taken to prevent contamination of the liquids in the washing vessels from this source, the whole apparatus being carefully wiped and the contents of each vessel transferred to marked stoppered bottles without opening the washing vessel at the conclusion of each day's work and similarly replaced at the beginning of the next. The apparatus was watched during the whole time so as to insure no accidental interference from the workers. The contents of each vessel were examined separately and the results showed that the air contained hydrochloric acid and chlorides of lead, zinc, tin and iron of which substances a tinner, even when using a bath provided with a hood connected to the furnace chimney, must inhale considerable quantities. It seems probable however that a considerable proportion of the chlorides of lead, etc. emanate not from the bath directly but from the tinned article as it is removed from the bath to the wiping stand. (See Experiment VIII.) The space between the diaphragms of the funnel of the absorption apparatus was empty in this experiment.

Experiment VII. This experiment is complementary to No. V and it is also comparable with Experiment IV. Its objects were—(a) To show the value of a respirator to a tinner. (b) To afford a basis for calculation of the danger to health of a tinner wearing a respirator but working at an open bath. (c) To afford some means of comparison

between the respective values of a respirator, and a hood with connection to the furnace chimney, to a tinner. The experiment was carried out in connection with the same bath as Nos. V and VI, the absorption apparatus being fixed in such a position inside the hood as to bring the mouth of the funnel about 3 ft. 10 ins. above the level of the molten metal, considerably to one side of the bath and just inside the apron partly closing the front of the hood. In this position the point from which air was aspirated was on the side of the bath opposite to the exhaust into the furnace chimney and was somewhat above breathing level. As in Experiment V, therefore, the results are probably lower than the average which would be obtained on an open bath, since the fumes were drawn away from the apparatus. Similarly the average amounts of deleterious substances inhaled by a tinner using an open bath would probably be considerably higher than those given as a result of this experiment. Hence it can only be taken as showing the minimum danger to health of a tinner wearing a respirator and using such a bath. It was however desired in this experiment to make the conditions distinctly unfavourable to the passage of the vapours through a glass wool filter. The space of three inches between the gauze diaphragms in the funnel of the absorption apparatus was filled with closely packed glass wool. The experiment was continued from day to day for five days and precautions were taken to avoid accidental contamination of the liquids in the washing vessel. As in Experiment IV difficulty was experienced in maintaining a passage for air through the glass wool filter, the fumes condensing in it and blocking it up. The contents of each washing vessel were separately examined and the results showed the air, even after passage through the glass wool, to contain hydrochloric acid and chlorides of lead, zinc, tin and iron. Experiment II showed that all dust could easily be arrested in the glass wool, and hence one is driven to the conclusion that the chlorides must exist in the air as vapour or in a state very closely approximating to that of vapour, though undoubtedly considerable quantities condense in the filter. The results also clearly show that it is not practicable for a tinner to use a respirator and that even if he could use it he would still inhale appreciable quantities of hydrochloric acid and chlorides of lead, zinc and tin, etc. though probably not to the same extent as a tinner using an open bath and no respirator but to a greater extent than one using a bath with hood and exhaust to the furnace chimney.

Experiment VIII. The object of this experiment was to—
(a) Ascertain the nature and extent of air contamination caused by

the operation of wiping excess of metal, while still in a molten state, from the tinned article. (b) To afford a basis for calculation of the effect of his work on the health of a wiper. The funnel of the absorption apparatus was connected with a large hood, made of thin sheet iron in the form of an inverted bucket, and was so placed that the lower edge of this hood was exactly on a level with the wiper's nose, the kettle being wiped being immediately under the centre of the hood. Aspiration was continued for six days. At the end of the experiment small particles of fibre, obviously derived from the tow used in wiping, could be observed in the first washing vessel but the closest examination could reveal none in the second. Occasionally during the experiment blue vapours could be seen rising from the hot tinned article and passing through the glass tubes of the absorption apparatus. The contents of each washing vessel were examined separately. Considerable quantities of metallic lead and tin, and fibre were found in suspension in the first washing vessel with chlorides of lead, zinc and iron in solution. In the second vessel no fibre nor metallic lead and tin was present though appreciable quantities of chlorides of lead, zinc and iron were found in solution. No hydrochloric acid was found in the free state in either vessel. In Experiment I it was noted that all dust was arrested in the first washing vessel and this is supported by the results of this experiment, all the solid matters being found in the first vessel and probably condensed vapour only provided the deleterious substances found in the second. The fact that particles of fibre are shown to float in the air is extremely important. They are produced during rubbing of the hot tinned surface of the kettle with tow and no doubt they collect minute quantities of metallic lead and tin and also of lead chloride, etc. before they become disseminated in the atmosphere. Indeed probably the whole of the metallic lead and tin and a small portion of the chlorides of lead, zinc, etc. found in the liquids of the absorption apparatus were carried into it by means of the small pieces of fibre. It at once becomes a question as to how much of the soluble lead (lead chloride) existing in the air of a tinning workshop is due to this. It will be seen later from a consideration of the results of examination of samples of dust that this is only small in all probability. The result of the experiment clearly showed that wiping is one of the most dangerous processes of tinning since not only is the wiper compelled to inhale considerable quantities of chlorides of lead, zinc, and iron as vapour, these being larger than those inhaled by a tinner using even an open

bath, but he will also inhale appreciable quantities of fibre carrying metallic lead and tin and chloride of lead.

In the following table the results of the workshop experiments are summarised.

TABLE VII.

Showing the quantities of deleterious substances found in the liquid of the absorption apparatus after passage of air aspirated from different points in a tinning workshop.

The percentage composition of the condensed fumes, etc. is shown by the figures in brackets below those giving the quantities of the various deleterious substances.

Experiment in which collected	Volume in cubic feet aspirated	Quantities, expressed in grams, of deleterious substances condensed in the absorption apparatus in each experiment										Ratio Tin Lead	
		In solution					In suspension					In sample	In original tinning mixture
		Chlorides of				Hydrochloric acid	Oxides of				Foreign matters (fibre etc.)		
		Lead	Zinc	Iron	Copper		Tin	Lead	Iron	Zinc			
V	27·2000	0·0039 (2·89)	0·0165 (12·21)	0·0068 (5·03)	Trace	0·1060 (78·46)	0·0019 (1·41)	—	—	—	—	0·5 1	1·22 1
VI	100·0300	0·0024 (7·08)	0·0155 (45·72)	0·0052 (15·34)	Trace	0·0090 (26·55)	0·0018 (5·31)	—	—	—	—	0·77 1	1·22 1
VII ¹	102·1200	0·0035 (1·13)	0·0077 (2·46)	0·0070 (2·24)	—	0·2940 (94·17)	—	—	—	—	—	Trace 1	1·22 1
Together with a small quantity of tin chloride													
VIII	67·2000	0·0128 (17·00)	0·0084 (11·15)	0·0061 (8·10)	—	Nil	0·0267 (35·46)	0·0153 (20·32)	—	—	0·0060 (7·97)	0·89 1	1·22 1
Together with a small quantity of tin chloride													

In the following table certain details as to volume aspirated, work done during the experiments etc. are shown.

¹ In this experiment the air before passing into the absorption apparatus was drawn through three inches of closely packed glass wool.

TABLE VIII.

Showing details of experiments.

Distinctive no. of exp.	Time of aspiration in hours		Duration of exp. in hrs.	Time in hours of aspiration during tinning of		Volume in cubic feet of air aspirated		Total volume of air aspirated in cubic feet	Temp. in degrees Fah. of air passing through meter		Barometric pressure in inches	
	When no tinning was in progress	During tinning and wiping		Kettles	Covers	When no tinning was in progress	During tinning and wiping		Maximum	Minimum		
Laboratory experiments :												
I	—	2 $\frac{2}{6}$	2 $\frac{2}{6}$ (1 day)	—	—	—	10·0000	10·0000	62·0	53·5	29·309	
II	—	5 $\frac{2}{6}$	5 $\frac{2}{6}$ (1 day)	—	—	—	20·0117	20·0117	68·9	59·0	29·242	
III	1 $\frac{2}{6}$	3 $\frac{2}{6}$	5 $\frac{2}{6}$ (1 day)	—	—	5·4500	8·5500	14·0000	61·0	54·5	29·321	
IV	1	4 $\frac{7}{6}$	5 $\frac{7}{6}$ (1 day)	—	—	1·5600	13·0200	14·5800	55·9	52·0	29·180	
Workshop experiments :												
V	21 $\frac{2}{6}$	5 $\frac{2}{6}$	7 $\frac{2}{6}$ (1 day)	3 $\frac{1}{6}$	2 $\frac{2}{6}$	8·4500	18·7500	27·2000	50·5	49·0	28·994	
VI	21 $\frac{2}{6}$	25 $\frac{2}{6}$	28 $\frac{4}{6}$ (5 days)	21 $\frac{2}{6}$	4 $\frac{2}{6}$	8·1800	91·8500	100·0300	66·8	50·9	29·143 to 29·529	
VII	6 $\frac{2}{6}$	22 $\frac{2}{6}$	28 $\frac{2}{6}$ (5 days)	20 $\frac{2}{6}$	2	24·2700	77·8500	102·1200	63·0	48·0	28·930 to 29·293	
VIII	—	24 $\frac{2}{6}$	24 $\frac{2}{6}$ (6 days)	24 $\frac{2}{6}$	—	—	67·2000	67·2000	71·9	58·1	29·249 to 29·716	

TABLE IX.

Showing the composition of a typical tinning metal and of the substance which collects as a pasty mass on the surface of the molten metal during tinning and from which vapours appear to emanate.

Nature of sample and how collected	Percentage composition		Ratio $\frac{\text{Tin}}{\text{Lead}}$	
	Soluble in water	Insoluble in water	In sample	In original tinning metal
Substance which collects as a paste on surface of tinning metal. Taken from surface of molten metal at conclusion of Experiment IV	Zinc chloride	34·28 %	4·91 1	1 1
	Lead chloride	4·63		
	Iron chloride	0·98		
	Tin oxide with trace of metallic tin	...		
	Zinc oxide	...		
	Lead oxide	...		
	Iron oxide	...		
Tinning metal. Taken from tinning bath at conclusion of Experiment VI	Chlorine (present as oxychloride)	...	1·22 1	—
	Loss, etc.	...		
	Metallic tin	...		
	Metallic lead	...		
	Metallic copper	...		
	Metallic iron	...		
	Metallic antimony	...		
Metallic zinc	...	Nil		
Metallic arsenic	...	Nil		

Distribution of deleterious substances in the atmosphere of a tinning workshop.

In order to form some conception of the manner in which air in different parts of the workshop is affected by the deleterious substances produced in tinning, samples of the dust, found deposited in all parts of the tinning workshop, were collected from selected points. In a good light it is possible to trace the general course of the fumes produced though this of course varies in different workshops. Usually, however, they appear to ascend to the roof immediately over their point of production without becoming disseminated to any great extent in the surrounding atmosphere. The workshop in which the experiments were made is very high and the blue vapours from the tinning baths and wiping stands appeared to rise directly upwards from their source of origin. In the upper part of the roof they appeared to mingle to some extent and then pass away through the large louvres provided. In the working portion of the atmosphere, *i.e.* for a height of 10 or 12 feet, vapour could only usually be observed in the immediate neighbourhood of the baths, etc. It was however impossible to say that dust (no doubt largely consisting of mineral matter produced in raking the fires) was more prevalent in one part of the atmosphere than another. Hence so far as ocular evidence can be trusted it appeared probable that all parts of the workshop are not equally dangerous. This point is emphasised by the result of Dr Legge's medical examination by which it was shown that while the men using a molten mixture of lead and tin were plainly affected by lead the worker using a pure tin bath in the same room was only slightly affected. The points from which the samples of dust were taken were selected with the object of testing the validity of this conclusion. The following table shows the point of collection and probable source of deleterious substances judged by ocular evidence of the course of the fumes. In taking the samples the whole of the dust from a selected area was removed, it was black in colour and appeared to contain considerable quantities of fibre similar to the tow used in wiping. A large proportion was however simply finely divided powder.

TABLE X.

Showing details of collection of dust samples.

Distinctive No. of Sample	Where collected	(a) Point from which collected	
		(b) Probable point of origin of deleterious substances	(4)
(1)	(2)		
10	¹ Tinning Work- shop A.	(a) Ledge of hood covering a common tinning bath, about 4 ft. 10 ins. above surface of molten metal, 5 ft. from wiping stand, and immediately in front of position of tinner during tinning.	
		(b) Fumes from tinning bath, fumes from articles when being removed from bath, and fumes and fibre from wiping stand.	
11	Do.	(a) Ledge of window between common tinning and pure tin baths 8 ft. 6 ins. from floor, the vertical line from this point to the floor being 5 ft. 6 ins. from the open front of the pure tin bath and 4 ft. 4½ ins. from the side wall of the common tinning bath and about 10 ft. from the wiping stand.	
		(b) Principally fibre from the wiping stand, with some fumes from the pure tin bath.	
12	Do.	(a) Window ledge 8 ft. 6 ins. from floor and immediately over the front of the pure tin bath, about 6 ft. above the surface of the metal.	
		(b) Fibre from the wiping stands and fumes from the pure tin bath.	
13	Do.	(a) Middle of a beam across middle of the workshop 13 ft. 6 ins. from the floor.	
		(b) Fibre and fumes from wiping principally, together with some fumes from each of the baths.	
14	Mounting Shop used in connection with Work- shop A.	(a) Middle of beam across middle of mounting shop 13 ft. 6 ins. from floor. Broken panes in windows between mounting and tinning shops allow passage of fumes from tinning shop.	
		(b) Fumes and fibre from wiping stands and a quantity of fumes from all baths which tend to collect in upper part of tinning workshop.	
15	Do.	(a) Ledge of fire-place behind moulder 5 ft. 6 ins. from floor.	
		(b) Dust from hammering of tinned kettles during mounting. This was the only sample collected which was free from fibre.	
16	Tinning Work- shop B.	(a) Blades of fan exhausting air by means of ducts and hoods from a point over the wiping stands, and also from a pure tinning shop in which no zinc chloride solution is used, but only molten tallow, for fluxing the metal, and hydrochloric acid for cleaning.	
		(b) Fumes and fibre from wiping stands.	
17	Do.	(a) Ledge of hood over common tinning bath, in workshop where a fan is used to exhaust air from a point above the wiping stands 5 ft. 6 ins. above surface of molten metal and immediately in front of position taken up by tinner during tinning, about 7 ft. from wiping stand.	
		(b) Fumes from bath, and fumes and fibre from wiping stand.	
18	Do.	(a) Beams just above a hood connected with ducts and fan exhausting air from above a wiping stand 4 ft. 3 ins. above lower edge of hood and 13 ft. 9 ins. from floor.	
		(b) Fumes and fibre from wiping stand, and fumes from common tinning bath.	
19	Do.	(a) Hole in wall 7 ft. above surface of molten metal and immediately over open front of a common tinning bath, direction of fan draught over wiping stand, however, tends to draw fumes away from this point.	
		(b) Fibre from wiping stand, and also fumes from tinning bath.	

¹ Tinning workshop A is that in which the experiments were carried out.

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In the following table the percentage composition of these samples is given :

TABLE XI.
Showing percentage composition of dust samples.

Dis- tinctive No. of sample	Where collected	Percentage composition											
		Soluble in water						Hydro- chloric acid	Insoluble in water				
		Chlorides of					Oxides of						
(1)	(2)	Lead (3)	Tin (4)	Zinc (5)	Copper (6)	Arsenic (7)	(8)	Tin (9)	Lead (10)	Zinc (11)	Copper (12)	Arsenic (13)	
10	¹ Tinning Work- shop A.	9.26	0.14	5.83	0.32	Trace	1.39	17.12	5.42	0.31	0.41	Trace	
11	Do.	0.11	Trace	0.79	0.08	Nil	0.11	9.56	5.83	0.28	0.30	Do.	
12	Do.	0.08	0.06	1.75	0.08	Do.	0.15	5.77	3.41	0.45	0.28	Do.	
13	Do.	0.71	Trace	2.56	0.25	Do.	0.82	8.72	6.17	0.28	0.12	Do.	
14	Mounting Shop.	0.20	Do.	2.11	0.17	Do.	0.50	7.09	3.71	0.24	0.12	Do.	
15	Do.	Nil	Do.	0.25	0.04	Do.	Nil	1.67	1.51	0.46	0.07	Do.	
16	Tinning Work- shop B.	7.31	0.05	1.64	0.33	Do.	0.57	9.22	2.37	0.05	0.15	Do.	
17	Do.	5.75	0.01	11.83	0.22	Do.	0.77	7.34	1.32	0.08	0.10	Do.	
18	Do.	17.19	0.03	6.94	0.19	Do.	2.25	21.94	2.72	0.11	0.11	Do.	
19	Do.	6.99	0.03	7.15	0.06	Do.	0.07	14.76	5.64	0.14	0.14	Do.	

¹ Tinning workshop A was that in which the experiments were carried out.

In considering the composition of samples of dust it would appear at first sight that this should approximate to that of fumes aspirated from a point near that from which the dust was taken. This is however not necessarily correct since in the experiments the fumes were condensed as a whole and therefore the results show their true composition, while if left to themselves they probably condense fractionally, those compounds like lead chloride condensing more quickly than others. Moreover the experiments show the fumes to contain a large proportion of hydrochloric acid, a gas which would not be deposited to any great extent since the samples of dust were quite dry in the ordinary sense. It is certainly a fact however that the result of Experiment VIII shows that the composition of the fumes, etc. produced in wiping does approximate to that of the sample of dust (sample 10) taken from a point in close proximity to the wiping stand, provided that the extraneous matters, *e.g.* mineral dust and fibre, etc., are eliminated by calculation. In the following table the composition of the deleterious substances which, when deposited with foreign matters, form dust

samples, is shown. The results have been obtained by eliminating by calculation all foreign matters. The results of Experiment VIII similarly treated are also shown for purposes of comparison.

TABLE XII.

Showing percentage composition of deleterious matters as they probably exist in the air before deposition as dust.

Dis- tinctive no. of sample.	Percentage composition of deleterious matters found in dust											Tin Ratio Lead	
	Soluble in water						Insoluble in water					In sample	In original tinning mixture
	Chlorides of					Hydro- chloric acid	Oxides of						
	Lead	Tin	Zinc	Copper	Arsenic		Tin	Lead	Zinc	Copper	Arsenic		
(exp.) 8	18.47	Trace	12.12	—	—	Nil	38.53	22.08	—	—	—	$\frac{0.89}{1}$	$\frac{1.22}{1}$
10	23.03	0.35	14.50	0.80	Trace	3.46	42.59	13.48	0.77	1.02	Trace	$\frac{1.14}{1}$	$\frac{1.22}{1}$
11	0.65	Trace	4.63	0.47	—	0.64	56.04	34.17	1.64	1.76	Do.	$\frac{1.37}{1}$	$\frac{1.22}{1}$ & $\frac{1}{0}$
12	0.67	0.50	14.67	0.67	—	0.42	48.37	28.58	3.77	2.35	Do.	$\frac{1.4}{1}$	$\frac{1.22}{1}$ & $\frac{1}{0}$
13	3.62	Trace	13.04	1.27	—	4.18	44.42	31.43	1.43	0.61	Do.	$\frac{1.1}{1}$	$\frac{1.22}{1}$ & $\frac{1}{0}$
14	1.41	Trace	14.92	1.20	—	3.54	50.14	26.24	1.70	0.85	Do.	$\frac{1.55}{1}$	$\frac{1.22}{1}$ & $\frac{1}{0}$
15	—	Trace	6.25	1.00	Trace	—	41.75	37.75	11.50	1.75	Do.	$\frac{0.94}{1}$	$\frac{1.22}{1}$
16	33.70	0.23	7.56	1.52	—	2.63	42.51	10.93	0.23	0.69	Do.	$\frac{0.95}{1}$	$\frac{1}{1}$?
17	20.97	0.03	43.14	0.80	—	2.81	26.77	4.82	0.29	0.37	Do.	$\frac{1.05}{1}$	$\frac{1}{1}$?
18	33.39	0.06	13.48	0.37	—	4.38	42.62	5.28	0.21	0.21	Do.	$\frac{1.12}{1}$	$\frac{1}{1}$?
19	19.98	0.09	20.44	0.17	—	0.20	42.20	16.12	0.40	0.40	Do.	$\frac{1.11}{1}$	$\frac{1}{1}$?

The results given in the two tables above are in many cases inconsistent. They however show that all parts of a tinning workshop are to a certain extent dangerous, and that points near the baths and wiping stands are exceedingly so (cf. samples 10, 17, 18 and 19). Samples 11 and 12 taken from a point remote from any source of lead fumes contain very little lead chloride though the influence of the pure tin bath is shown by the proportion of zinc chloride in the two samples and also by the increase in the ratio of tin to lead. Generally it appears from a study of the tables that the fumes do cling to the part of the workshop in which they are produced, this being most strikingly shown by the

decrease in the lead chloride found in those samples taken from a point remote from a source of lead fumes. The proportion of insoluble lead is fairly regular in all the samples taken from any particular workshop though it evidently varies under different conditions in different workshops. Thus in workshop B it is much lower than in workshop A while the proportion of lead chloride is generally higher. In the former, however, air was exhausted from the wiping stands and also from the pure tinning shop by means of a fan and main trunk with hoods over each stand. Probably a large quantity of the fibre produced in wiping is removed by this means but the construction and position of the exhaust was such that while not sufficiently strong to remove all the fumes produced during wiping it would yet have a considerable tendency to draw fumes out of the hood, covering the tinning bath, into the workshop. The effect is shown by the greatly increased proportion of lead chloride and decreased percentage of metallic lead though probably the tinning metal used which is richer in lead may have some effect in causing the difference. In general however the fan has a good effect since it was noticeable that much less dust was deposited than in any other workshop visited and the movement of air was sufficiently great to reduce very considerably the quantities of deleterious substances present in a given volume of air. The good effect is also shown by the low proportion of cases of lead poisoning occurring in this workshop. In workshop A the proportion of fibre was apparently about the same in all the samples and this is supported by the quantity of insoluble lead found in those samples (11, 12 and 13) not much affected by any source of fumes. The proportion of lead chloride found in these samples throws some light on the question of the quantity of this compound carried by fibre floating in the atmosphere. Assuming, as seems probable, that nearly all the insoluble lead found in the dust is carried by such fibre and putting down the whole of the lead chloride found in samples 11 and 12 as coming from this source it will be seen that the proportion of lead chloride in the atmosphere mechanically carried on fibre is very small as compared with that due to fumes or vapour near the tinning baths and wiping stands (cf. samples 11 and 12 with samples 8 and 10) and does not amount to more than $\frac{1}{40}$ or $\frac{1}{50}$ of the quantity of insoluble metallic lead carried in the same way and found in the dust samples or in Experiment VIII. The insidious nature of the fumes is shown by sample 14 taken from the mounting shop, they having apparently leaked from the tinning workshop through broken windows situated at a height of about 14 feet in the wall dividing the

two workshops. From a consideration of the composition of this sample, especially of the ratio of tin to lead, it is apparent that fractional deposition of the fumes must take place. Sample 15 shows there is a certain amount of danger from mounting, appreciable quantities of metallic tin and lead dust being produced by the hammering. A further point brought out by the examination of samples of dust is that compounds of copper, probably resulting from the chemical action of the flux and acid on the brazed part of the article being tinned, and also of arsenic, probably originating as impurity in the acid used, must exist in the air of tinning workshops.