

THE CHEMICAL AND PHYSICAL INVESTIGATION OF GERMICIDAL AEROSOLS

I. GERMICIDAL SMOKES

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(With 8 Figures in the Text)

INTRODUCTION

IN a previous paper (Twort, Baker, Finn & Powell, 1940) we were able to show that the bactericidal properties of phenolic aerosols were correlated with their physical characters, though our experiments were not sufficiently numerous or varied to enable us to estimate separately the effect of the different factors operative. Here we propose to describe similar tests which we have carried out on the germicidal smokes used by Twort & Baker (1940, 1941), namely, those produced by smouldering cardboard impregnated with potassium nitrate, and by dropping incense and Peru balsam on to hot metal surfaces. There were also used mixtures obtained by distilling Peru balsam under reduced pressure: fraction I, b.p. 109–110° C.; fraction II, b.p. 120–138° C.; fraction III, b.p. 148–155° C., at 3 mm. Hg, and the residue from this operation.

It will be realized that owing to the heterogeneous nature of the starting materials and the difficulty of controlling the conditions of production, these smokes form much less tractable experimental material, from the physical point of view, than simple mixtures of pure substances atomized in a definite way, and the results must accordingly be of less general interest and significance.

The size distribution in smokes produced by volatilization and subsequent condensation is very greatly affected by the rate at which the newly formed aerosol is diluted, e.g. by fanning or blowing; the more rapid the dilution, the finer the smoke, for the particles are very minute and therefore highly mobile when first formed, so that if the particulate volume is small, coagulation is rapid. The rate at which the vapour leaves the hot surface will similarly affect the particle size. If, further, the vapour is a mixture of substances with different volatilities, the particles are unlikely to grow at the same rate, or to have the same composition, the dilution also affecting the condensation. For these reasons the particles in any one such smoke will differ among themselves as regards physical behaviour, and are, in fact, found to do so. On the other hand, the bacteriological tests refer to the smoke as a whole.

PARTICLE SIZE AND EVAPORATION OF SMOKES

The size of a smoke particle is generally determined by measuring its rate of fall under gravity, and its evaporation by repeating the measurement at short intervals. The detailed technique and apparatus have been described previously (Twort *et al.* 1940). When a particle is so small that its fall under gravity is obscured by its Brownian motion, its size can still be estimated by making use of the latter property (cf. Perrin, 1909) if at the same time it is not evaporating noticeably. In such cases we adopted the following method.

The eyepiece of the ultramicroscope is fitted with a graticule ruled in squares, calibrated against a stage micrometer for the various objectives in use. At equal intervals of time (usually every 10 sec.) for some minutes the position of a selected particle in the field is read as its displacement in a horizontal direction from the central vertical line of the graticule. (It will be noted that atmospheric pressure transients and any displacement of the air in the ultramicroscope cell required to keep the particle in view will have little effect on the horizontal movements.) Then the differences between the successive pairs of readings are squared and the average of the squares is taken and divided by the time interval; this mean square velocity is connected with the radius by Einstein's (1905, 1906) relation:

$$\frac{\overline{x^2}}{t} = \frac{RT(1 + AL/r)}{3\pi\eta rN},$$

where x = any displacement, $\overline{x^2}$ = mean square displacement, t = time interval, R = gas constant, T = absolute temperature, A = a constant ≈ 0.86 , L = mean free path of medium (air), N = Avogadro's number, η = viscosity of medium, r = radius of particle. For example, readings were taken at 10 sec. intervals on a droplet of non-volatile mineral oil for 20 min. The mean square displacement was found to be 4.4 units of the graticule (each equivalent to 1.477×10^{-3} cm.). Hence the mean square velocity was 0.89×10^{-6} cm.²/sec. η was taken to be equal to $10^{-4} \{1.81 - 0.0049(20 - \theta)\}$ c.g.s. units, where θ = temperature in degrees Centigrade = $25^\circ \text{C.} = 298^\circ$ absolute, $AL = 8 \times 10^{-6}$ cm., $R = 8.314 \times 10^7$ ergs/degree and $N = 6.06 \times 10^{23}$. This gives a value for the radius of the droplet of

$$r = 0.33 \mu.$$

The radius of the same particle was also estimated by the gravitational fall method; the average time of fall through a distance of 2.954×10^{-2} cm. (20 lines of the graticule) was 18.71 sec., giving a velocity of fall of

$$1.577 \times 10^{-3} \text{ cm./sec.}$$

The Stokes-Cunningham relation

$$V = \frac{2gpr^2(1 + AL/r)}{9\eta}.$$

(where V = fall velocity, g = gravitational acceleration, ρ = density of droplet, here = 0.901) then gave a value for r of

$$0.32\mu.$$

Two other particles gave values for r of 0.24 and 0.35 μ by the first method and 0.29 and 0.35 μ respectively by the second. In order to carry out determinations of both types on the same particle, the same microscope objective had to be used throughout, its magnification a compromise between those which would normally have been chosen as the most suitable for the two methods. In view of this the agreement between the pairs of values for the radii is regarded as satisfactory.

The smokes from cardboard, and the residue from Peru balsam dropped on to a brass block at 250° C., agreed in consisting of large numbers of very fine particles; they coagulated quite rapidly until many of the finest had been removed, the larger particles increasing up to 0.2 μ radius by condensation or collision with amicros during a few minutes. But the average size at the time of formation was much less than this, and in the dilutions used in bacteriological experiments would be maintained for a much longer period. The particles did not appear to evaporate.

The smoke from incense was exceedingly heterogeneous as regards particle size and showed correspondingly rapid coagulation. Particles as large as 1 μ radius were found, though the vast majority were much smaller (0.3 μ), and evaporated noticeably, at a rate estimated to be of the order of 10^{-11} cm²/sec. (i.e. a 1 μ particle of the smoke would evaporate in about 3 hr. if this rate were maintained).

Peru balsam consists of benzyl esters of benzoic and cinnamic acids, the free acids themselves, vanillin, together with esters of complex alcohols and resinous substances. These latter, forming a brittle amorphous mass, constitute the residue from the dry distillation of the balsam, and yield only a tenuous smoke when heated to 300° C. The distilled fractions contain only small amounts of these substances, and are readily volatilized; in them subsists the greater part of the germicidal activity of the balsam.

The evaporation of typical particles in smokes from the whole balsam and the three fractions is represented in Figs. 1-4, showing the decrease of fall velocity and radius with time. The smokes were in all cases produced by dropping the substances on to a brass block heated to 250° C., a horizontal jet of air being at the same time directed across the surface to dilute the smoke. It will be seen that, except perhaps in the case of fraction II, there is no continuous relation between the form of the evaporation curve and the initial size of the drops—the latter is very difficult to observe owing to the presence of compounds which evaporate too rapidly for measurements to be made. As mentioned above, this is the behaviour to be expected of smokes formed by condensation of mixed vapours.

There is, however, a certain type of agreement. With fraction I (Fig. 1) the

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approximate parallelism of the earlier parts of the curves is evident, but the amount of involatile residue seems to vary fortuitously. Since the first and

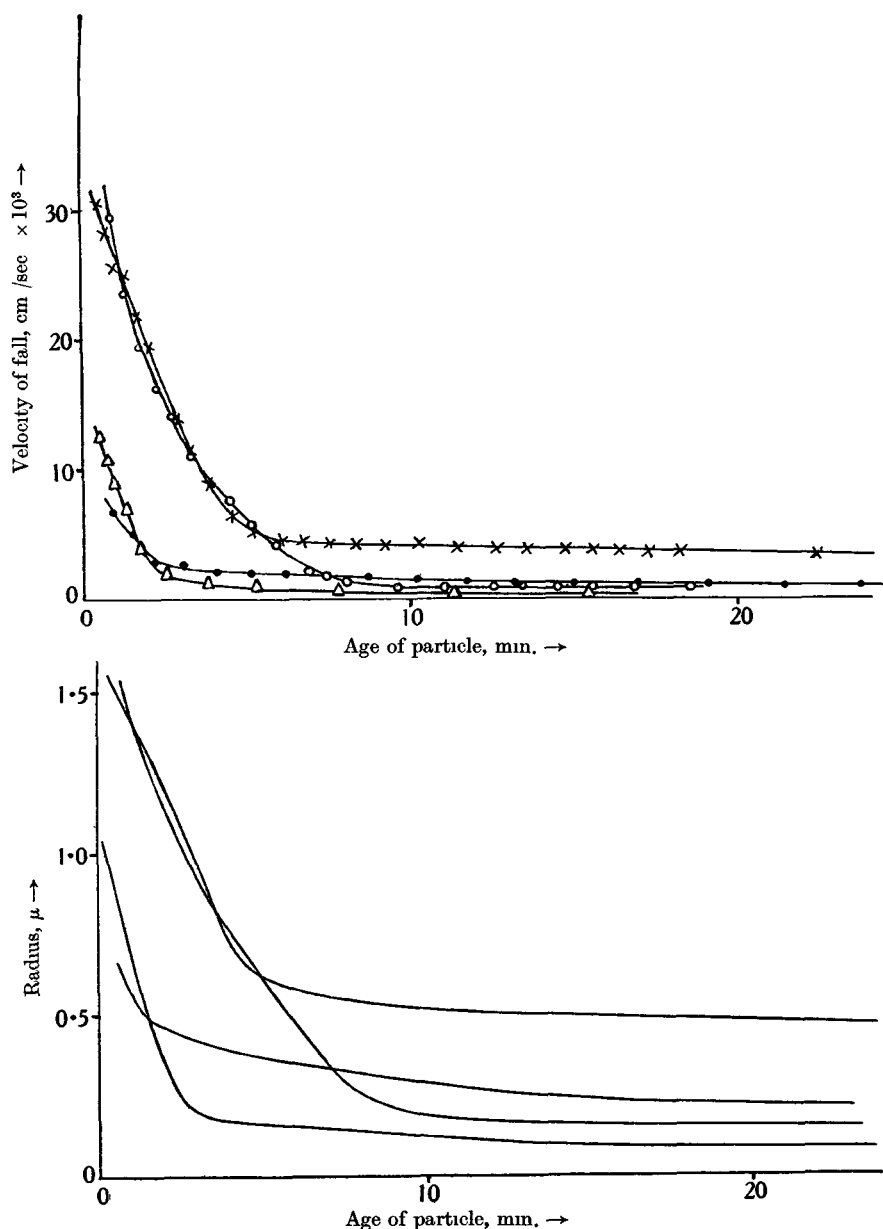


Fig. 1. Evaporation of smoke of Peru balsam, fraction I. From brass at 250° C.

second phases of evaporation are rapid, the germicidal activity of the smoke must be largely ascribed to these residual particles which have been observed to persist for 45 min. without change.

The balsam itself (Fig. 4) shows the same effect; in addition, the evaporation is prolonged in some cases by a slow change prior to the attainment of the final residual size.

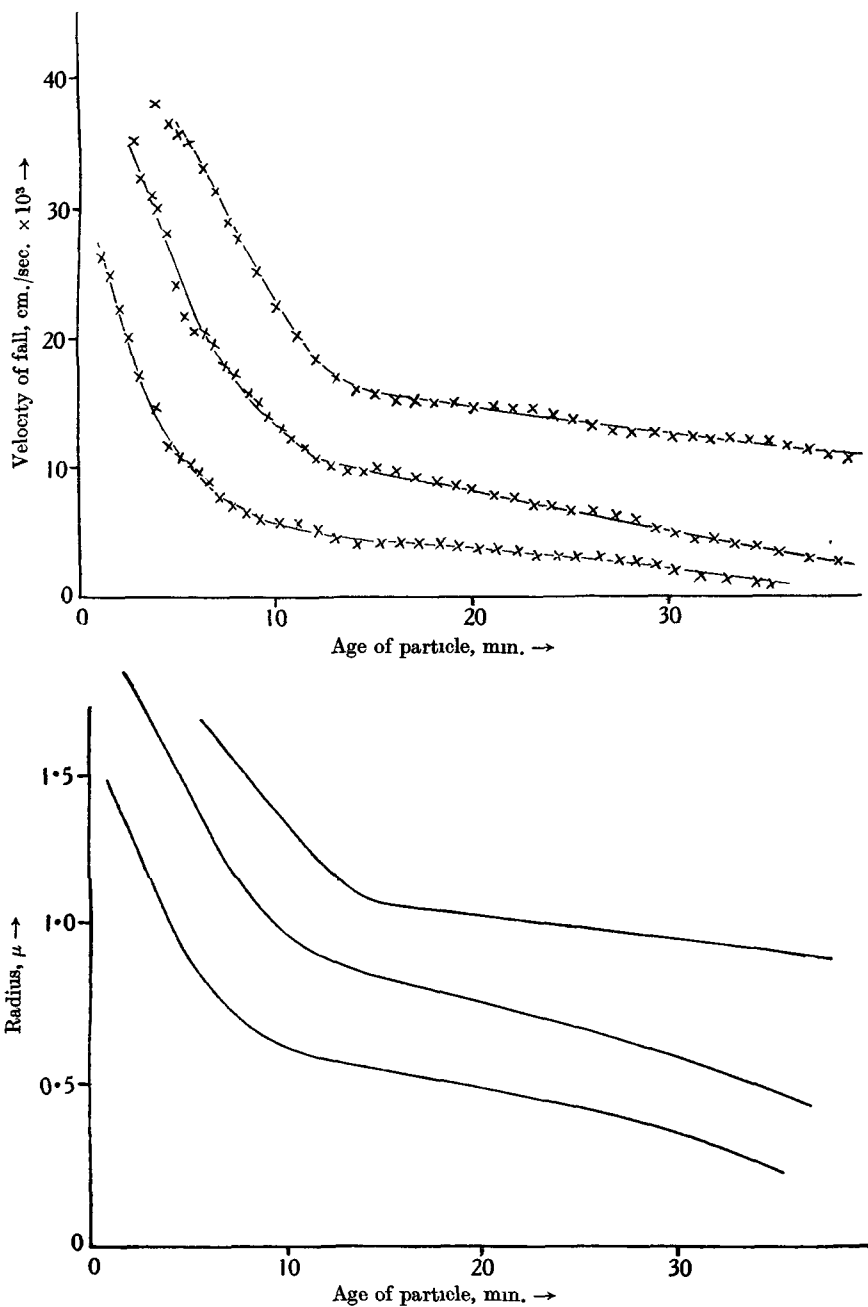


Fig. 2. Evaporation of smoke of Peru balsam, fraction II.

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Fraction II (Fig. 2) behaved more regularly. Evaporation took place in two stages, the second at a nearly constant rate. It was noteworthy that the particles often evaporated completely, unlike fraction I, and when residues

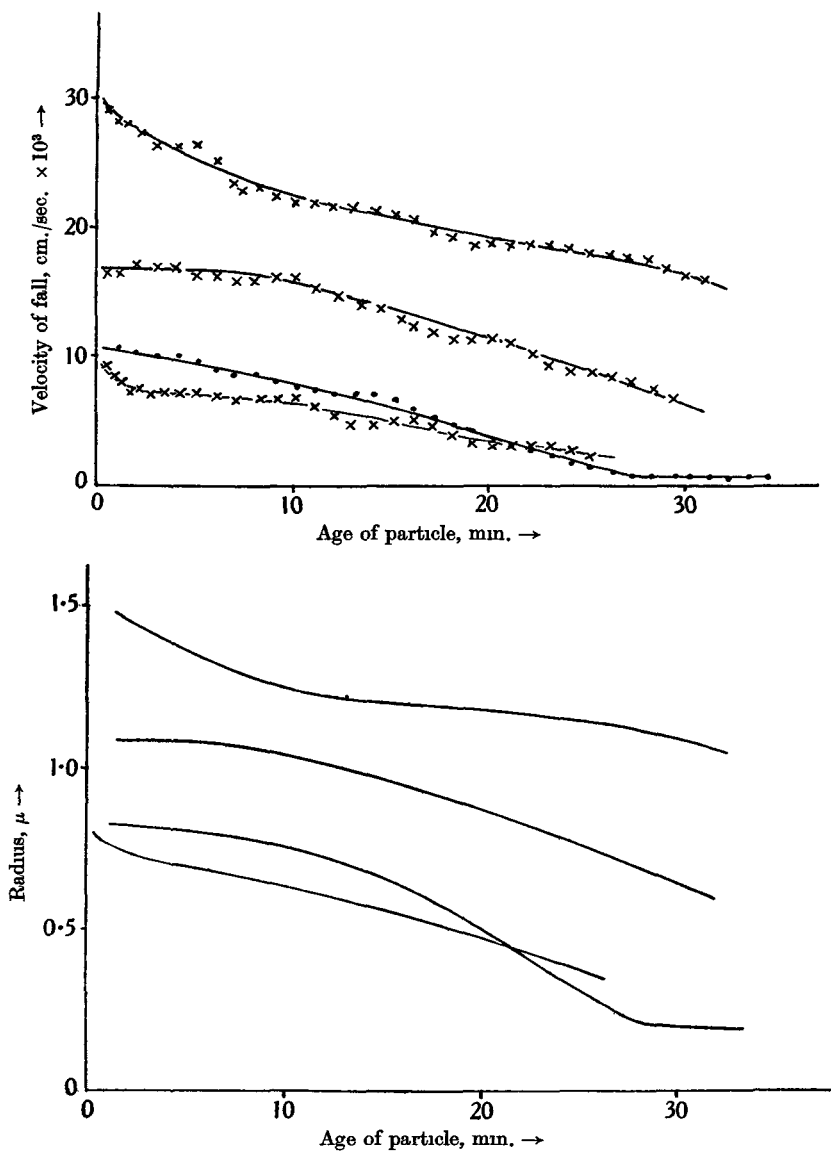


Fig. 3. Evaporation of smoke from Peru balsam, fraction III.

were found they were so small as to be ascribable to impurities picked up from the air.

The smoke from fraction III was much coarser than the others in this group. While the particles evaporated slowly, they did so completely in most

cases, again unlike fraction I. The form of the evaporation curves is here very inconstant (Fig. 3).

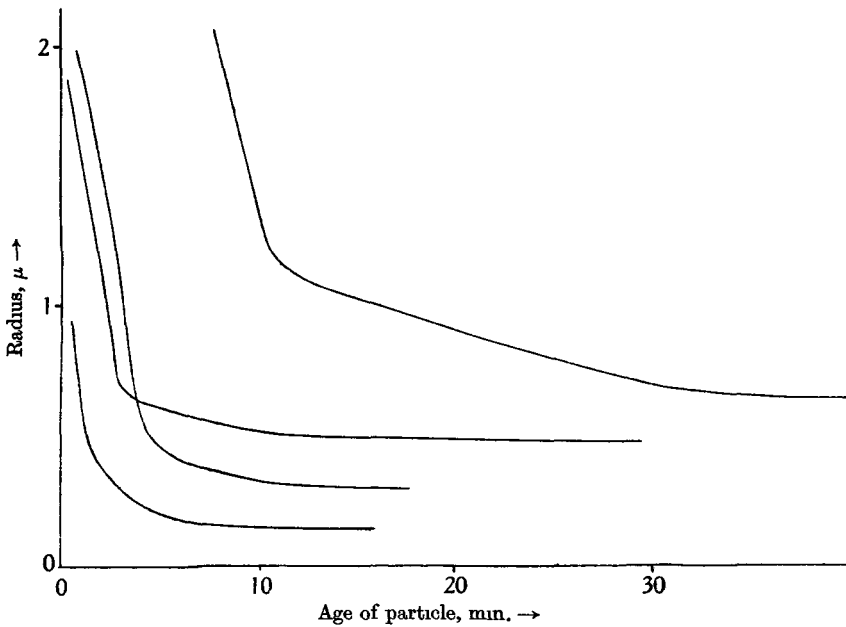
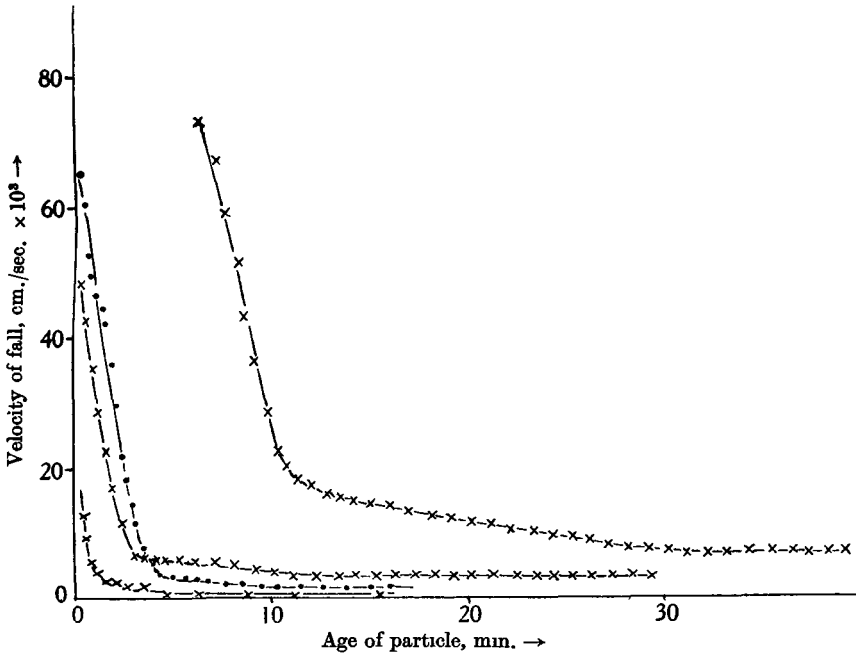


Fig. 4. Evaporation of smoke of Peru balsam.

It was felt on consideration of these results that the behaviour of fraction I was anomalous, on account of the high proportion of involatile matter in the smoke particles. This was unlikely to have been present initially; it might have been carbonaceous, and formed pyrogenetically, or it might have contained copper or zinc derived from the brass heating block. It was found that the latter was appreciably corroded by fraction I, the molten mixture quickly becoming green in contact with it; the green compound was soluble in chloroform and was thus possibly volatile at the temperature of the block. Three experiments were carried out to test these suppositions. First, the smoke was produced from fraction I by using a glass instead of a brass surface. Secondly, the smoke was formed by heating the substance in a platinum boat inside a small electric furnace (Fig. 5); a current of air carried the vapours through a

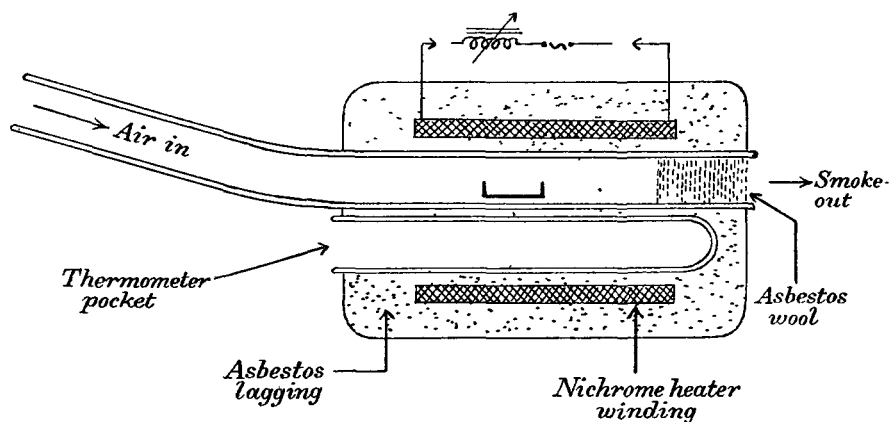


Fig. 5. Electric oven for blown smokes. Scale 1/1.

filter, consisting of a plug of asbestos wool, before escaping into the air and condensing. The results of examination of the smokes thus formed were inconclusive. Persistent residues were found in both cases, smaller than before on the average, and fewer particles left residues which were a large enough fraction of their original volume to be definitely regarded as not due to dust collected from the air (Figs. 6, 7). Thirdly, an attempt was made to detect metallic compounds in the smoke; the latter formed by volatilization from a brass surface was passed through a filter, and the material collected was washed out with alcohol and acetic acid. After evaporation of the solvent, organic matter was destroyed by boiling with sulphuric acid, and tests for copper applied to the solution. In none of nine trials was it found.

Lastly, an aerosol was made from fraction I by atomizing a solution in alcohol (Fig. 8). The evaporation was substantially the same as with the heat-produced smokes, the residues however being rather less persistent than those of the smoke made by volatilizing from a brass surface.

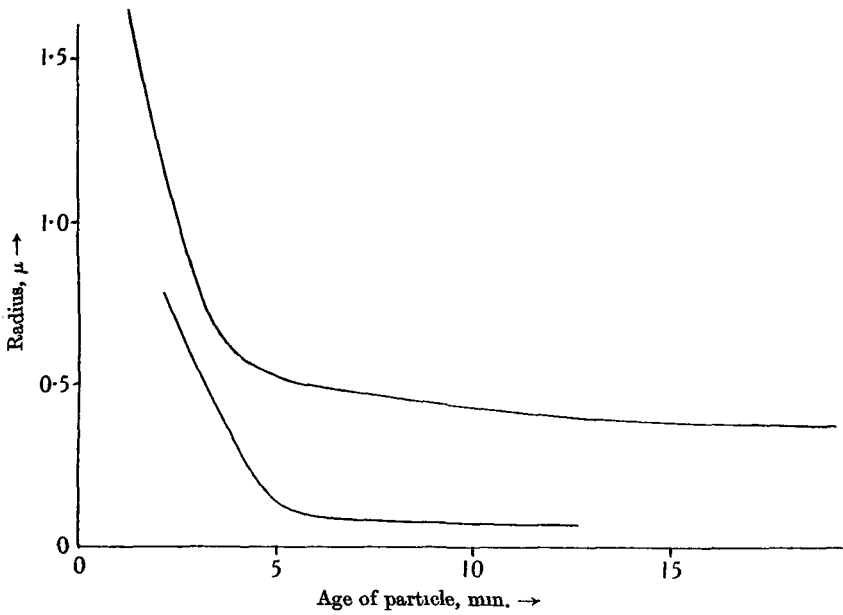


Fig. 6. Evaporation of smoke of Peru balsam, fraction I. From glass at 250° C.

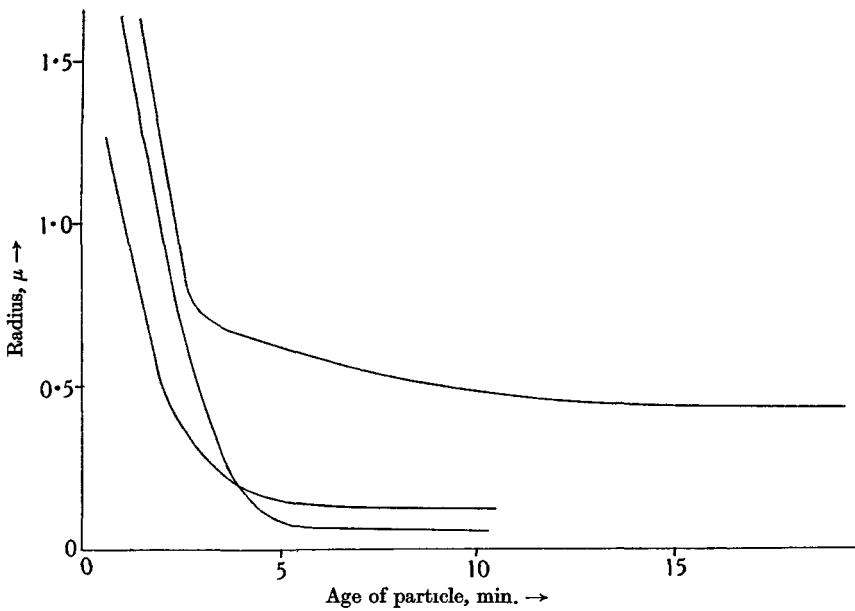
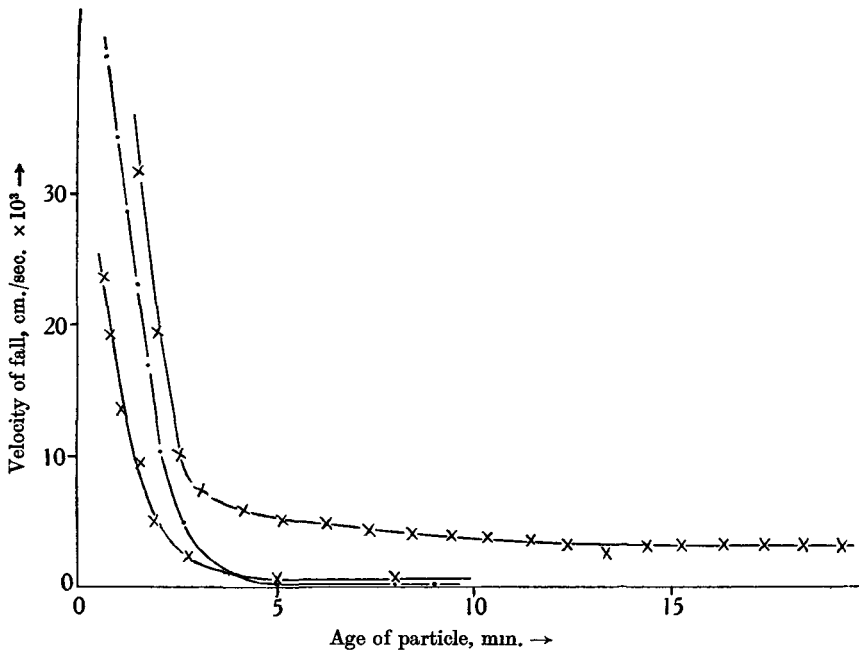


Fig. 7. Evaporation of smoke of Peru balsam, fraction I. From platinum at 250°C Filtered.

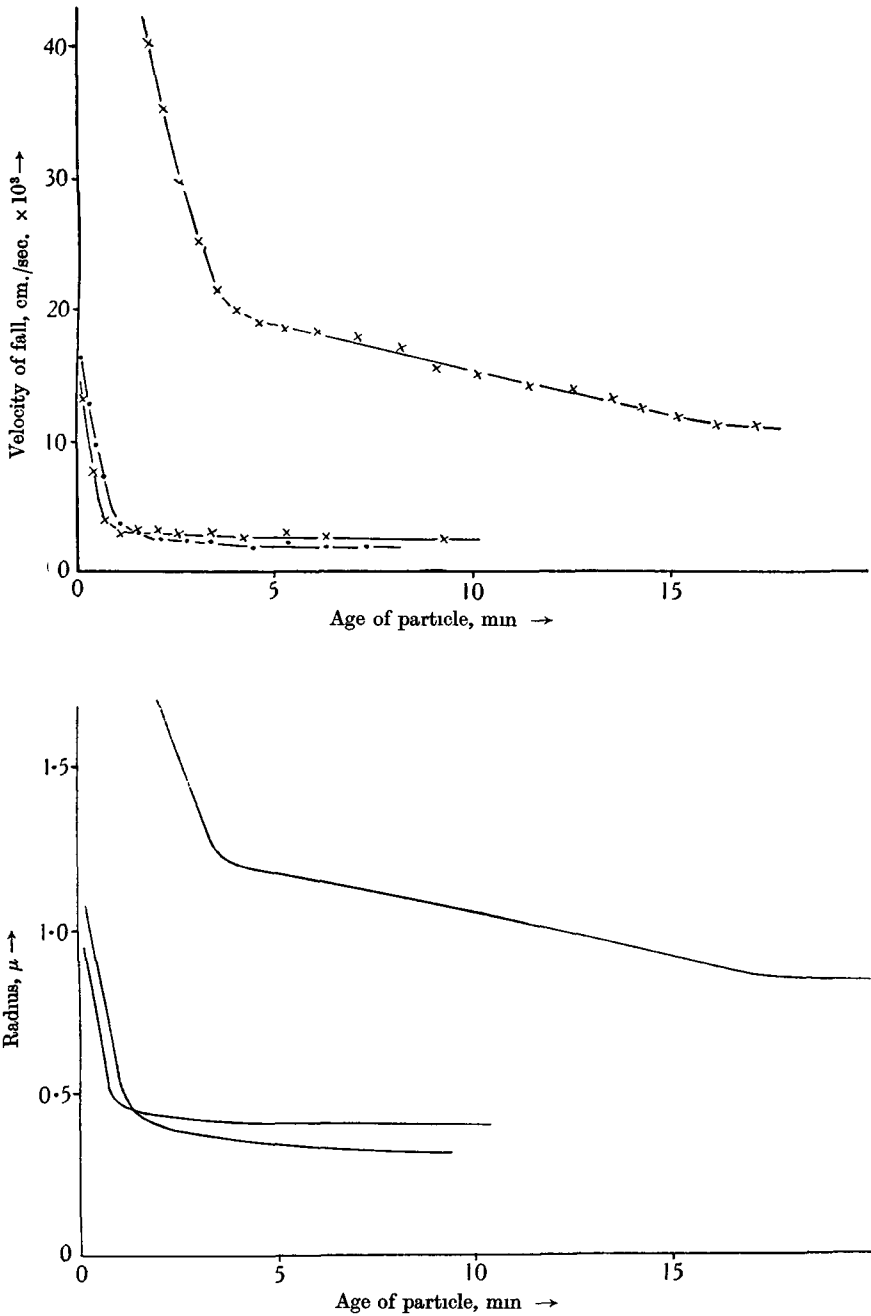


Fig. 8 Evaporation of droplets of Peru balsam, fraction I. From an atomized solution in alcohol.

PURE SUBSTANCES

In connexion with the Peru balsam smokes we have determined the evaporation rates of particles of the following substances: benzoic acid, cinnamic acid, benzyl cinnamate and vanillin. (That of benzyl benzoate has already been measured. Twort *et al.* 1940.) In working out the experimental data (velocities of fall under gravity) for pure substances, it has been found convenient to introduce a fictitious velocity V_M , such that

$$V_M = \frac{2gr^2\rho}{9\eta}.$$

Actually
$$V = \frac{2gr^2\rho}{9\eta} (1 + AL/r).$$

Hence
$$\Delta V = V - V_M = -\frac{K^2\rho}{2} + \sqrt{\left(\frac{K^4\rho^2}{4} + K^2\rho V\right)},$$

where
$$K = AL\sqrt{\frac{2g}{9\eta}}.$$

In view of the small value of ΔV , η was taken as constant and equal to 1.80×10^{-4} c.g.s. unit. ΔV was plotted on a graph against V for various values of ρ . The experimental values for the velocity were corrected to V_M by deducting the appropriate ΔV , and V_M plotted instead of V , against the age of a particle. Then if the particle evaporates according to the linear law $ds/dt = \text{constant}$ ($s = \text{surface area of droplet}$), dV_M/dt is constant, since $V_M \propto r^2 \propto s$. The four substances mentioned were found to follow this relation within the limits of experimental error, and dV_M/dt was simply obtained from the experimental points by the method of least squares.

Aerosols of vanillin, cinnamic acid, and benzyl cinnamate were formed both by volatilization and by atomizing solutions; both methods gave concordant results in each case.

On the first occasion on which benzoic acid was examined, the aerosol was made by heating, and dV_M/dt was found to be -2.79×10^{-3} cm./sec.², the mean of eight agreeing values. On three subsequent occasions, dV_M/dt was found to be much greater and more variable (-6×10^{-3} cm./sec.² very approximately) for particles produced both by atomizing and by heating. We have not been able to repeat the original result. Since benzoic acid was then introduced for the first time into the microscope room, it might have been expected that supercooled liquid droplets were measured in the first instance, and afterwards crystalline particles; but the apparent reversal of these conditions was surprising. It was noticed that on cooling drops of fused benzoic acid 1–2 mm. in diameter, nests of needles up to 5 mm. in length were formed, so that it seemed possible that the original result did in fact refer to the supercooled liquid, the second to solid particles of such extremely irregular shape that the effective radius was high and the effective density was low.

In order to obtain an unequivocal value for the evaporation rate of solid benzoic acid, measurements were made on particles 1–2 mm. in diameter. These were formed by cooling drops of the liquid on the tips of fine glass rods and a nearly spherical shape was obtained by repeatedly melting the surface, to a smaller extent each time, in a current of hot air. Each drop was suspended in the centre of a flask containing a little powdered caustic soda and kept at 60° C. Measurements of diameter in four directions were made from time to time, and the surface calculated from the mean square of these values. They led to a value for ds/dt of -4.0×10^{-7} cm.²/sec. at 60° C. A value for ds/dt at 22° C. can be deduced from this. From Langmuir's (1918) formula

$$-\frac{ds}{dt} = \frac{8\pi DMp}{RT\rho},$$

where D = diffusion coefficient of the vapour, M = molecular weight and p = vapour pressure,

$$\frac{(ds/dt)_{60}}{(ds/dt)_{22}} = \frac{D_{60} p_{60} 295}{D_{22} p_{22} \cdot 333} \text{ approximately,}$$

where the subscripts refer to the temperatures. We may take $D \propto T^2$, and by extrapolation of the vapour-pressure data for benzoic acid, we find

$$\frac{p_{60}}{p_{22}} \simeq 55 \text{ for solid, and } \left(\frac{ds}{dt}\right)_{60} / \left(\frac{ds}{dt}\right)_{22} = 62,$$

corresponding to a $(dV_M/dt)_{22}$ of -7.7×10^{-4} cm.³/sec.² The lower of our two previous results is 3.8 times this. If the latter refers to liquid droplets, we should have

$$\left(\frac{dV_M}{dt}\right)_{\text{liquid}} / \left(\frac{dV_M}{dt}\right)_{\text{solid}} \simeq 4.0.$$

But this ratio is equal to $p_{\text{liquid}}/p_{\text{solid}}$, given by the relation

$$\log \frac{p_{\text{liquid}}}{p_{\text{solid}}} = \frac{\Lambda}{R} \left(\frac{1}{T} - \frac{1}{m} \right) + \frac{k}{2} \left(1 - \frac{m}{T} \right) + \frac{k}{2} \log \frac{m}{T},$$

where Λ = latent heat of fusion at the melting point (m) = 1.73×10^{11} ergs/mole and k = temperature coefficient of Λ , taken as 13 cal./mole/degree (Sidgwick, 1932), whence the ratio of fall velocity gradients should be about 4.3. The agreement between these values must be considered reasonably good, since differences in ρ have been neglected, and the value for k is an average which may be incorrect; accordingly our first value for dV_M/dt is taken as that of the supercooled liquid.

Table 1 gives a synopsis of these results. The rate of decrease of surface with time (ds/dt) is to be regarded as characteristic for the substance since it is independent of the radius of the droplet. Where the density of the latter is in doubt (as in the case of a highly supercooled liquid), the quantity $\rho ds/dt$ has been calculated from dV_M/dt instead. A more easily visualized quantity is the time (τ) taken by a 1μ radius droplet to evaporate completely.

Table 1. *Evaporation rate of small particles*

Substance	State of aggregation	Temp. of determination ° C	Density	$-dV_M/dt$	$-ds/dt$	$-\rho ds/dt$	τ sec.
Vanillin	(Liq.)*	26.2	—	1.10×10^{-3}	—	1.05×10^{-8}	ca. 11
Cinnamic acid (trans)	Solid	21.2	1.25	1.24×10^{-5}	1.05×10^{-10}	—	1190
Benzyl cinnamate	Liq.	28.7	1.11†	1.33×10^{-5}	1.29×10^{-10}	—	970
Benzoic acid	Liq.‡	22.1	—	2.8×10^{-3}	—	3.0×10^{-8}	ca. 5
	Observed	Solid	60	—	4.0×10^{-7}	—	—
Calculated	Solid	22	(1.27)	7.7×10^{-4}	6.4×10^{-9}	—	20
Benzyl benzoate (for comparison)	Liq.	23.0	1.12	2.65×10^{-4}	2.49×10^{-9}	—	50

* Assigned on grounds of probability only

† Value for supercooled liquid.

‡ Assigned by comparison with calculated value for solid

The above values for dV_M/dt are the mean of several series of observations and the temperatures the means of those obtaining in the different series. These figures must be taken with some reserve at present, since the temperature in the ultramicroscope cell is not known with certainty, and dV_M/dt is found in some cases to have a very high temperature coefficient. For example, benzyl benzoate has $\tau = 81$ sec. at about 18°C ., and $\tau = 50$ sec. at about 23°C .

DISCUSSION

The above results call for little comment from us. Taken in conjunction with the bacteriological data obtained by our colleagues, Twort & Baker, they agree with a previously expressed hypothesis, that other things being equal, a germicidal aerosol is the more effective the less volatile are its particles, and, less generally, the smaller they are, up to a certain ill-defined limit, Twort & Baker find that the effectiveness of the aerosols from Peru balsam fractions is in the order, fraction I (maximum), fraction II, residue, fraction III; those from incense and cardboard are also remarkably useful. There are, however, a number of factors connected with the method and conditions of formation of these smokes which are not easily controlled and which, therefore, make it impossible to give a definite statement of the relationship in this very complicated instance. Here bacteriological methods are more sensitive than physical.

Tests have been carried out on the germicidal activity of some of the more volatile components of Peru balsam. They are relatively inefficient. The activity of the smokes is thus due to the residual non-volatile particles; unfortunately these are the least accessible to chemical investigation.

If smokes of this type can be produced having a potency approaching that of mechanically atomized germicides, it is clear that they offer a cheap and ready means of air disinfection on a small scale. However, practical developments have yet to wait upon the consideration of toxicity, odour and so on.

Among the values for the evaporation of the pure substances mentioned, that for cinnamic acid appears outstanding. It is surprisingly low. Benzoic acid evaporates about two hundred times as fast as cinnamic acid, and sixteen times as fast as its benzyl ester, whereas cinnamic acid appears to be less volatile than its benzyl ester. The difference seems to be too great to be due to the effect of larger molecular weight and size, and may possibly be accounted for by the action of light on the particles of cinnamic acid, with formation of at least a surface layer of the dimmer, α -truxillic acid. It is known that the radiation responsible for this change lies in the near ultra-violet and visible, and that glass and water are fairly transparent to it (Stobbe & Lehfeldt, 1925). The very concentrated light beam in the ultramicroscope cell may reasonably be supposed to contain sufficient energy in this part of its spectrum to effect the change to the minute extent necessary. Accordingly, the evaporation rate given for cinnamic acid in Table 1 should be regarded as tentative only until further experiments have been carried out; an investigation of the anomaly is in progress.

SUMMARY

Smokes formed by heating Peru balsam and incense, and by smouldering cardboard, have been examined with the ultramicroscope; the sizes and evaporation of their particles have been measured. It is found that the particles in such smokes frequently differ in properties from one particle to the next.

The radii of very small particles have been estimated by measurements of their Brownian motion.

In view of the bacteriological data, the germicidal activity of the smokes is ascribed to the less volatile constituents and the smaller particles.

The evaporation rates of a number of pure substances have been determined.

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