

Fig. 2.

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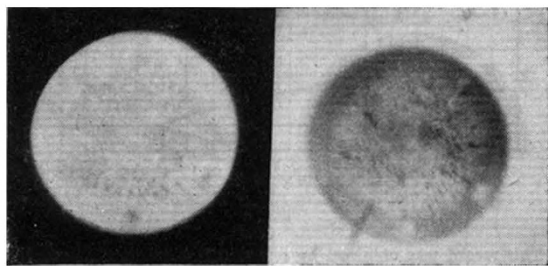
¹ Diamond, Hinman, Dunmore and Lapham, *J. Res. Nat. Bur. Stand.*, **25**, 327 (1940).

² Simpson, G., and Scrase, F. J., *Proc. Roy. Soc., A*, **161**, 309 (1937).

Origin of Ion Burn in Cathode-Ray Tubes

CERTAIN types of cathode-ray tubes in which the luminous spot on the fluorescent screen is moved by magnetic fields are liable to a peculiar defect, known as 'ion spot' or 'ion burn'. It is now thought that in most cases they are due to ions issuing from the thermionic cathode. This conclusion was mainly reached by inference from the composition of the ion stream which was analysed by mass-spectroscopic methods by several investigators.^{1,2,3}

Several 'ion burns' were found in this laboratory which showed distinctive patterns corresponding to the electron emission patterns of the thermionic cathodes as observed by using the cathode-ray tubes as 'electron-microscopes' (in the type of tube investigated, this can be done by simply switching off the focus coil and deflecting coil currents, and operating the tube otherwise under normal conditions). This appears to establish a direct experimental proof that 'ion burns' are, although not necessarily in all cases, due to negatively charged ions emitted from the electron emissive parts of the thermionic cathode, and that in particular local 'ion burn' density and specific electron emission of the corresponding part of the cathode may be closely related.



'ION BURN' (a) AND ELECTRON IMAGE OF CATHODE (b). REDUCED TO 3/5.

A good example of this kind of 'ion burn' is shown by the accompanying photographs. It was observed that in a certain freshly made cathode-ray tube, using magnetic deflexion and magnetic focusing and a tetrode gun system, an 'ion burn' with a distinct pattern seemed to form fairly rapidly when the cathode was overheated for reactivation while the accelerating voltage was left on. In order to intensify the 'ion burn', the tube was operated for three hours with an accelerating voltage of 6 kV. and a beam current of 600 microamp., but running the heater with 9.0 V. instead of 6.3 V. as usual, leaving the focusing coil switched off but a small scan applied to the deflecting coils, so that the pattern of the electron emission image of the cathode was suppressed. After this period the 'ion burn' had become just discernible at the normal accelerating voltage of 6 kV. On lowering the voltage to 1 kV. the 'ion burn' stood out in good contrast on the background of the even illumination of the undamaged part of the fluorescent screen when scanned with a slightly diffuse electron beam. Photograph a was taken under these conditions.

The accelerating voltage was then raised again to 6 kV., and focus coil and scan were switched off, leaving all other conditions as during

the three hours previous run, so that a magnified electron emission image of the cathode was obtained on the tube screen (photograph b). It will be noticed that the marked 'electron emission structure' of the thermionic cathode is reproduced (in negative) by the 'ion burn' except for a few, though perhaps significant, details. For example, the 'ion burn' image contains an additional fairly intense dark spot near the centre which has no counterpart in the 'electron emission' image. Such additional rather intense but small 'ion burns' near the centre of the large main 'ion burn' are frequently observed in magnetically focused cathode ray tubes although their origin appears obscure at present.

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¹ Bachman, C. H., and Carnahan, C. W., *Proc. Inst. Rad. Eng.*, **26**, 529 (1938).

² Broadway, L. F., and Pearce, A. F., *Proc. Phys. Soc. (London)*, **51**, 385 (1939).

³ Schaefer, H., and Walcher, W., *Z. Phys.*, **121**, 679 (1943).

Quenching of Fluorescence by van der Waals Forces

THE quenching of fluorescence of dyes in solutions has been explained satisfactorily as a chemical reaction in a number of cases. In an interesting paper¹ Weiss has classified some different mechanisms of 'chemical' quenching, such as quenching by ions and by the electro-negative oxygen molecule². Furthermore, Weiss has attempted to explain the well-known fact of concentration quenching chemically: according to him the formation of dimers is responsible for the decrease of fluorescent efficiency in solutions with increasing concentration of the fluorescing solute. On the other hand, Franck³ has shown that under certain conditions the electronic energy of an excited dye molecule in solution may serve to form a tautomer by a process of internal conversion. In this way electronic energy is transferred into vibrational energy of nuclei and so the fluorescent efficiency is reduced.

It should be emphasized, however, that the process of quenching in solutions is of a very general nature. The fluorescent yield of anthracene in the solid state is more than 80 per cent, but was shown by Bowen and Norton⁴ to be reduced to a fraction of this value in different solvents, chemically inert solvents forming no exception to this rule. One should therefore look for a physical interpretation of the phenomenon which would account for its general validity.

Such an interpretation presents itself when one considers that a fluorescing molecule in a solvent of a very dilute solution interacts with the molecules of the solvent in the same way as they interact with each other. Apart from the thermal energy, this interaction is mainly determined by van der Waals forces, the influence of which manifests itself in both the absorption and fluorescence spectra of the molecule⁵. There is the well-known red shift of these spectra in solution as compared with the gaseous state which is of the order of 10^3 cm^{-1} ; secondly, the peak of the longest wave absorption band is separated from the peak of the shortest wave fluorescence band, this (0—0) separation being of the order of 10^4 cm^{-1} ; and, finally, there is a broadening of the bands.

Quantitatively, all these three factors run parallel with each other and they can be related to the van der Waals interaction of the fluorescing molecule and the molecules of the solvent. Partly this interaction (in dipole-free liquids) is proportional to the polarizability of the solvent; partly it is determined by the synchronized oscillations induced in one molecule by the changing field due to the time-varying configuration of charges of another molecule. This latter factor is proportional to a term containing a dispersion denominator, and therefore may reach considerable values in case of resonance.

With an experimental arrangement similar to that described by Rollefson and Dodgen⁶, and which will be described elsewhere, it was found that quenching of fluorescence is another effect of van der Waals interaction which may be quantitatively related to those mentioned above. Obviously the van der Waals forces, by distorting the normal charge distribution of the molecules, increase the probability of a conversion of the electronic excitation energy of the fluorescing molecule into vibrational energy of its neighbours. According to this explanation, quenching should become more pronounced the closer the main absorption frequency of the solvent approaches the characteristic absorption frequency of the fluorescing molecule. Concentration quenching or self-quenching easily fits into this picture, being the special case of complete resonance, when the excited molecule interacts with molecules of the same kind.

Measurements were made on anthracene ($1 \times 10^{-4} \text{ mol./l.}$) in hexane and benzene which were freed from air by distillation *in vacuo* and sealed off; the photographic-photometric method was used for absorption as well as for emission. Only the Hg-lines at 3650 Å. which do not excite any of the solvents were allowed to pass through the cells containing the solutions and the pure liquids respectively. As the shortest wave fluorescence band of anthracene was strongly absorbed in the experimental arrangement used, the sum of the intensities of the second and third band was determined and related to the absorbed energies. This is a correct procedure, since it was proved experimentally that the relative intensities of the bands do not depend on the nature of the solvent⁷.

The results show that fluorescence of anthracene is quenched in benzene by 35 per cent as compared to the solution in hexane. This is in disagreement with the figures given by Bowen and Norton⁴, who found the efficiency in benzene higher than in hexane by about 20 per cent. This discrepancy may possibly be explained by the fact that the anthracene concentrations as used by these authors were 25 times as high as ours. Here self-quenching may already play a part⁸, acting more strongly between the anthracene molecules in hexane, the viscosity of which at room temperature is half that of benzene.