203. *The Available Surface of Cellulose.*

By O. Rhys Howell and Albert Jackson.

In the preceding communication an account is given of the absorption spectrum of solid anhydrous cobalt chloride deposited on various supports, including filter-paper. It was deemed of interest to measure the absorption spectrum with different amounts of the deposited solid, since this might afford a novel method of determining the available or real surface of cellulose fibre.

The paper used was made in the Department of Textile Chemistry of this College from a batch of good cotton cellulose originally intended for nitration. The material received only moderate beating, and no addition was made to the "furnish." The paper is therefore composed purely of cotton cellulose. It is an absorbent paper similar to that commonly employed for filtration and is therefore referred to throughout as filter-paper.

Pieces of the filter-paper, all of the same area (10 sq. in.), were impregnated with the same volume (1·5 c.c.) of aqueous solutions of cobalt chloride of different concentrations.

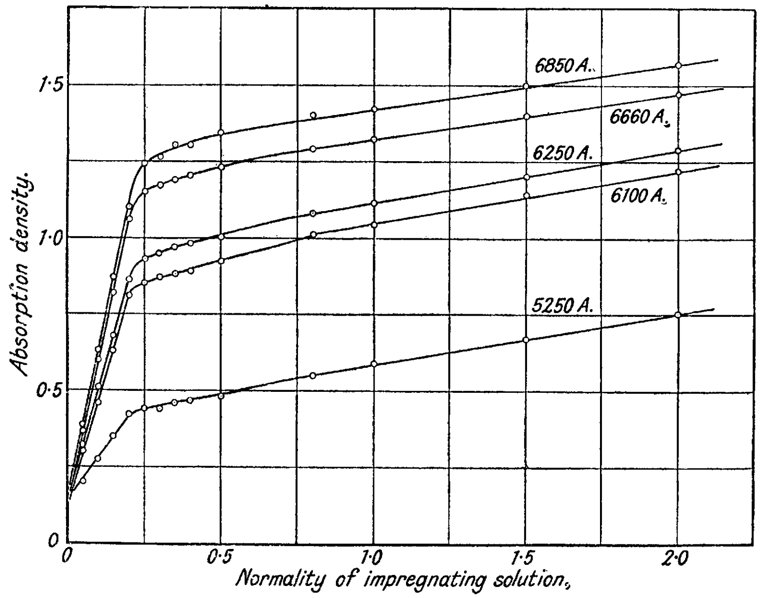
Table I.

	Extinction coefficient at (A.).				
$CoCl_2$, *N*.	6850.	6660.	6250.	6100.	5250.
0·05	0·39	0·37	0·32	0·30	0·20
0·10	0·63	0·60	0·51	0·46	0·27
0·15	0·87	0·82	0·68	0·63	0·35
0·20	1·10	1·06	0·86	0·81	0·42
0·25	1·24	1·15	0·93	0·85	0·44
0·30	1·26	1·17	0·95	0·87	0·44
0·35	1·30	1·19	0·97	0·88	0·46
0·40	1·30	1·20	0·98	0·89	0·47
0·50	1·34	1·23	1·00	0·92	0·48
0·80	1·40	1·29	1·08	1·01	0·55
1·00	1·42	1·32	1·11	1·04	0·59
1·50	1·50	1·40	1·20	1·14	0·67
2·00	1·57	1·47	1·29	1·22	0·75

Each piece was dehydrated and introduced into the air-tight moisture-free cell, where its absorption spectrum was measured in the manner already described.

Results.—The absorption spectrum of one of the specimens is reproduced and discussed in the previous communication. The general form of the curve is precisely similar for every specimen; it is independent of the amount of cobalt chloride present, but the intensity of the whole absorption increases with increasing deposition of the salt.

The scale readings (densities) at the four chief bands of the blue form and at the band of the red form for each concentration of solution used for impregnation have been read from the curves; they are given in Table I and plotted in the figure.



Discussion.—From the figure, it is seen that with increasing amount of cobalt chloride the absorption at first increases very rapidly and then gradually merges into a linear relation over which the increase is quite small. Over the initial portion of the curve the surface of the filter-paper is evidently being progressively covered with a primary film of the solid; over the final portion the continued increase in absorption is evidently due to the increasing thickness of deposit. The point at which the two portions intersect is the same for all the bands, *viz.*, at 0·24N-aqueous cobalt chloride solution for impregnation, and this must be very approximately the stage at which the surface first becomes covered.

The number of molecules of cobalt chloride deposited on the filter-paper from the known volume of solution of this critical concentration can be calculated. The area occupied by each chloride molecule in the crystal lattice layer can also be calculated. Hence, on the assumption that when the surface is first covered the film of solid is a unimolecular layer corresponding to a single layer of the crystal lattice, the area on which it stands, *i.e.*, the available surface of the filter-paper, can be determined. The requisite data are in Table II.

TABLE II.

Size of filter-paper used = 10 sq. in.	= 64·52 cm.^{2}
Volume of solution used for impregnation	= 1·50 c.c.
Critical concn. of impregnating solution from curve of extinction coefficient	= 0·24N
No. of $CoCl_2$ molecules in this volume = 6·06 × 10^{23} × 1·5 × 10^{-3} × 0·12	= 10·9 × 10^{19}
Area of one $CoCl_2$ molecule in the crystal lattice layer	= 10·9 A.^{2}
Real area of the filter-paper, assuming single lattice layer of $CoCl_2$ = 10·9 × 10^{19} × 10·9 × 10^{-16}	= 1·19 × 10^5 cm.^{2}
Weight of the filter-paper (10 sq. in.)	= 0·877 g.
Available surface per g. = 1·19 × 10^5/0·877	= 1·36 × 10^5 cm.^{2}
Apparent surface of fibres per g.	= 1·6 × 10^3 cm.^{2}
Ratio (Available surface)/(Apparent surface)	= 85

The value for the available surface thus obtained, 1·36 × 10^5 cm.^{2}/g., is a maximum value; if the initial coating is multimolecular, the value must be divided by the number of lattice layers constituting the deposit.

The filter-paper used in this investigation has been examined microscopically by Mr. F. W. Bailey, M.Sc.Tech., whom we desire to thank. Two hundred separate pieces of fibre were measured; splitting of the fibres had occurred to a limited extent during beating, and the total apparent surface (including that of the canals) was calculated by using the value 0·621 for the specific volume of cotton cellulose in water (Davidson, *J. Textile Inst.*, 1927, **18**, T175). The value thus found is $1·6 \times 10^3$ cm.^{2}/g. (compare Bell, "The Effects of Beating on Fibrous Cellulose," Thesis, Edinburgh University; Strachan, *Proc. Tech. Sect. Paper Makers' Assoc.*, 1926, **6**, 139; Herzog, *Papier-Fabr.*, 1925, **23**, 121; *Naturwiss.*, 1924, **12**, 955). The available surface is therefore about 85 times as great as the apparent surface.

The available surface of wood cellulose has been measured from the absorption compression of water (Stamm, *J. Physical Chem.*, 1929, **33**, 398); the value found is $3·1 \times 10^5$ cm.^{2}/g., which is 170 times as great as the apparent surface calculated from microscopical observation (see also Mark, " Physik und Chemie der Cellulose," Berlin, 1932, pp. 163 and 182, for ramie fibre).

These figures are of the same order as those now obtained for cotton cellulose, and afford strong evidence for the truth of the assumption on which they are based, *viz.*, that the initial coating of the solid cobalt chloride consists of a single layer of the crystal lattice.

The original layer may not be wholly continuous. It is seen from the curves that there is a transitional portion before the linear relation begins, and it is possible that over this range the spaces between the almost continuous unimolecular layer are being closed by overlapping of the layers subsequently deposited. The linear relation begins at a concentration about three times as great as that necessary for the production of the original layer, so that (on this assumption) three lattice layers suffice to secure a wholly continuous deposit. Alternatively, it may be argued that the effect of the layers immediately next after the original unimolecular layer is greater than that of those subsequently deposited, and that, after the deposit is about three layers thick, each additional layer produces an approximately equal effect.

It is difficult to compare the change of absorption with concentration for cobalt chloride and that for dyes on textiles (see, *e.g.*, for wool, Cunliffe and Lambert, *J. Soc. Dyers Col.*, 1929, **45**, 313; for cotton, Guelke and Fitzsimons, *Trans. Faraday Soc.*, 1934, **30**, 512). The concentration of vat dyes used (*e.g.*, Blue RC, Blue 3G, Blue GCD, Ciba Blue 2B) reached a value of 2—3%. The number of molecules per g. of cotton present over the range examined is considerably less than for cobalt chloride; for instance, 1% of Ciba Blue gives $1·0 \times 10^{19}$ molecules/g. as against $1·25 \times 10^{20}$ molecules/g. of cobalt chloride for the original unimolecular layer. Little is known, however, regarding the orientation of dyes on fibres. The molecules of the vat dyes are very large; if we consider only the benzene nuclei, each with an area of 24 A.^{2}, those mentioned above have areas 10 or 20 times that of the cobalt chloride molecule. Therefore, if the molecules are lying flat, the surface they cover is comparable with that of the cobalt chloride in these experiments. If, however, they are oriented wholly or partly vertically, or if they are present in colloidal form, the covering of the surface may not be nearly so complete as that attained with cobalt chloride. Further, the mechanism of the deposition of dyes is not likely to be as simple as that of cobalt chloride, since these substances do not possess the simple layer lattice and have a specific affinity for the fibre.

It is hoped, however, that similar measurements to those now reported will shortly be made with dyes, and that these may yield some information on the molecular occupation of the surface.

A new theory of the structure of cellulose has recently been advanced (Farr and Eckerson, *Contr. Boyce Thompson Inst.*, 1934, **6**, 189, 309; Farr and Sisson, *ibid.*, p. 315; Farr, *Paper Trade J.*, 1935, **101**, T.A.P.P.I.Sect., 183; Farr and Eckerson, *Textile World*, 1936, **86**, 74; Farr, *J. Appl. Physics*, 1937, **8**, 228). It has been demonstrated that in the young cotton fibre there are discrete particles or granules of cellulose, and that as the fibre develops, these arrange themselves into a series of long chains. The particles are covered with and cemented together by a pectic material, the volume of which is an almost negligible part (only about 1%) of the whole. By dissolving away this cementing medium, the particles constituting the mature fibre can be separated and examined. It is found that " one of the most impressive properties of a mass of particles is their uniformity in size." The particles are about 1·5 μ long and about 1·1 μ broad; they are roughly ellipsoidal in form.

It is interesting to compare the apparent surface of these particles with the available surface found in this investigation. The requisite data are collected in Table III. The particle is regarded as a true ellipsoid of major axis, $a = 1{\cdot}5\ \mu$, and minor axes, $b = c = 1{\cdot}1\ \mu$; the eccentricity $e = \sqrt{(a^2 - b^2)/a^2} = 0{\cdot}68$. The volume of the pectic binding is neglected.

TABLE III.

Dimensions of particle $= 1{\cdot}5\mu \times 1{\cdot}1\mu \times 1{\cdot}1\mu$
Volume of particle $= 4/3 \times \pi\mu^3 \times 1{\cdot}5/2 \times 1{\cdot}1/2 \times 1{\cdot}1/2 = 9{\cdot}5 \times 10^{-13}$ cm.^{3}
No. of particles per c.c. $= 1/9{\cdot}5 \times 10^{13} = 1{\cdot}05 \times 10^{12}$
No. of particles per g. $= 1{\cdot}05/1{\cdot}6 \times 10^{12} = 6{\cdot}56 \times 10^{11}$
Surface of particle $= 2\pi b^2 \,(1 + \sin^{-1} e/e\sqrt{1 - e^2}) = 2\pi \times 1{\cdot}1^2 \times 2{\cdot}49\mu^2 = 4{\cdot}72 \times 10^{-8}$ cm.^{2}
Surface per g. $= 6{\cdot}56 \times 10^{11} \times 4{\cdot}72 \times 10^{-8} = 3{\cdot}10 \times 10^4$ cm.^{2}/g.
Ratio (Available surface)/(Particle surface) $= 1{\cdot}36 \times 10^5/3{\cdot}10 \times 10^4 = 4{\cdot}4$

It is seen (Table III) that the available surface of cellulose is about 4·4 times as great as the surface of the particles regarded as smooth ellipsoids. The particles are, however, known to be composed of micelles of glucose residues and the available surface may well be several times as great as that of smooth particles of the same dimensions.

It may be noted that if the particles are present in the fibre in the same form as in the free state, even the maximum closeness of packing would require a higher value for the amount of cementing medium than that actually observed. If the packing of the particles results in distortion, the surface would be thereby increased and give a somewhat smaller value for the ratio of the available surface to the smooth particle surface.

SUMMARY.

1. The absorption spectrum of solid anhydrous cobalt chloride deposited in different amounts on filter-paper has been measured.
2. The absorption at the maxima of the five best-defined bands has been plotted against the amount of cobalt chloride deposited.
3. All the curves are of precisely the same form and exhibit discontinuity corresponding to the formation of a primary covering.
4. Reasons are given for assuming that this primary coating is unimolecular, *viz.*, a unit layer of the crystal lattice.
5. On this assumption, the area occupied by the cobalt chloride, *i.e.*, the available surface of the filter-paper, has been calculated.
6. The total apparent surface of the filter-paper (calculated from measurement of the constituent fibres under the microscope) is $1{\cdot}6 \times 10^3$ cm.^{2}/g. The available surface is $1{\cdot}36 \times 10^5$ cm.^{2}/g., which is 85 times as great.
7. The value is a maximum one. If the primary film is multimolecular, the value must be divided by the number of unit crystal lattice layers constituting the deposit.
8. The magnitude of the value in relation to the granular theory of cellulose is discussed.

THE COLLEGE OF TECHNOLOGY, MANCHESTER.

[*Received, May* 10*th*, 1937.]