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TRANSACTIONS

28.—THE MEASUREMENT OF THE FLUIDITY (OR VISCOSITY) OF COTTON IN CUPRAMMONIUM SOLUTION

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1. INTRODUCTION AND SUMMARY

The measurement of the rate of flow of cellulose solutions, in addition to possessing fundamental importance, has proved of great value in controlling the chemical processing of cellulose textiles, and in diagnosing the causes of deterioration in cotton and other cellulose materials. The viscometer now widely used for the measurement is of the type described by Clibbens and Geake[1]. It is a capillary instrument, and was specially designed to simplify the technique of measurement for a system very sensitive to the presence of atmospheric oxygen, since the necessity—imposed by earlier methods—for working in an atmosphere of nitrogen greatly reduces the practical utility of the measurement as an industrial control method. The simplification involved some sacrifice of features generally accepted as desirable in the design of capillary viscometers; for example, the capillary discharges directly into air, and its ratio of length to diameter is smaller than would normally be used.

The method of expressing the result of the rate of flow measurement chosen by Clibbens and Geake was the fluidity in c.g.s. units of a 0·5% cellulose solution in a standard cuprammonium solvent. The complete fluidity scale for cellulose solutions then extends from a value of about 2, for cotton cellulose purified by the mildest methods, to about 70, the fluidity of the pure solvent. The part of the scale of interest in cotton technology is restricted to a range from about 2 to 40, since the chemical degradation of the cellulose corresponding to this upper limit is accompanied by almost complete mechanical disintegration of the cotton fibre. The normal cellulose rayons have fluidities of about 40 in 0·5% cellulose solution, and progressive chemical attack of the material corresponds to a range of fluidity from this value up to about 60, at which point rayons have lost so much in strength as to render them impossible to handle as continuous threads. The fluidity of rayons is, however, generally measured in 2% solution, when the range of 40 to 60 for 0·5% solutions is lowered to a range from about 7·5 to 35—

very similar to the range of interest in cotton processing. The advantage to practical viscometry of confining attention to the same numerical fluidity range for cotton and rayon is very great.

Recommendations for a standard method of measuring and expressing the rate of flow of cellulose solutions for industrial control purposes have recently been made in a report by the Fabrics Co-ordinating Research Committee of the Department of Scientific and Industrial Research[2]. This report contains a precise specification for a viscometer of the pattern described by Clibbens and Geake, and gives detailed instructions for its use, closely following the methods of those authors. The recommended form for expressing the result is again as the fluidity in c.g.s. units of a 0·5% cotton solution, or a 2% rayon solution.

Since 1927 many hundred viscometers substantially as described in the earlier paper have been made and calibrated in the laboratories of the British Cotton Industry Research Association for use in the textile industry. This paper amplifies the earlier descriptions in the light of the large experience thus gained. The viscometers now being made are called " X-type," and they are constructed to a specification almost identical with that given in the report of the Fabrics Research Committee, except that the use of KPG precision bore capillary permits a stricter specification of the capillary diameter. The detailed calibration of the viscometers is described, and the calibration results for 200 X-type instruments are analysed. The analysis shows that the specification is satisfied in practice, and that the flow of true viscous liquids in the X-type viscometer is expressed with reasonable accuracy by the Poiseuille Law. Pure phenyl ethyl alcohol is suggested as an ultimate reference standard for the calibration of viscometers suitable for fluidity measurements in the range of principal interest. Further observations are recorded showing that the deviation of the flow of cellulose solutions from the Poiseuille Law diminishes with falling concentration of a given cellulose sample, and with increasing chemical degradation of the cellulose. This effect of chemical degradation in causing the solution to approximate more closely to a true viscous liquid was first shown by Clibbens and Geake (*loc. cit.*), though the fact has apparently escaped notice by some later workers (cf. Sakurada[3]).

The composition, density and fluidity of the standard cuprammonium solvent now used in these laboratories are given. The composition follows the recommendation of the Fabrics Research Committee, and corresponds to a lower ammonia content than the solvent used by Clibbens and Geake.

The application of fluidity measurement for detecting the source of damage to defective cotton goods is described in one or two particular cases. The requirements sometimes necessitate the measurement of fluidity with much smaller samples of cotton than those needed for observations with 0·5% solutions in the capillary type of viscometer (0·1 gram). To meet these special requirements a rolling sphere viscometer has been designed suitable for use with 0·5% solutions when only 0·01 gram of cellulose is available; the instrument, its calibration, method of use and limitations are described.

Data are recorded for the effect of heat on the fluidity of cotton containing various acids and salts. The most satisfactory method for showing that finished cotton goods are free from " injurious chemicals " likely to cause deterioration of the cellulose during storage is by means of fluidity measurement before and after subjecting the cotton to a standard heat treatment.

2. THE B.C.I.R.A. STANDARD CAPILLARY VISCOMETER (X-TYPE)

(a) Specification and Method of Use.

The construction of the viscometer is shown in Fig. 1, and it only differs in detail from the construction described in the earlier paper[1]. The long wide glass tube A forming the upper portion, which also serves as the dissolution vessel for the cellulose, is provided with four rings etched round its circumference. Of these, the topmost G merely defines the depth of insertion of the rubber stopper, and thus determines accurately the enclosed volume of solution. The three other rings are timing marks, and the fluidity of the solution is calculated from the time of flow between B and D, the top and bottom timing marks. Observations at the intermediate timing mark C serve to detect any considerable irregularity due to partial choking

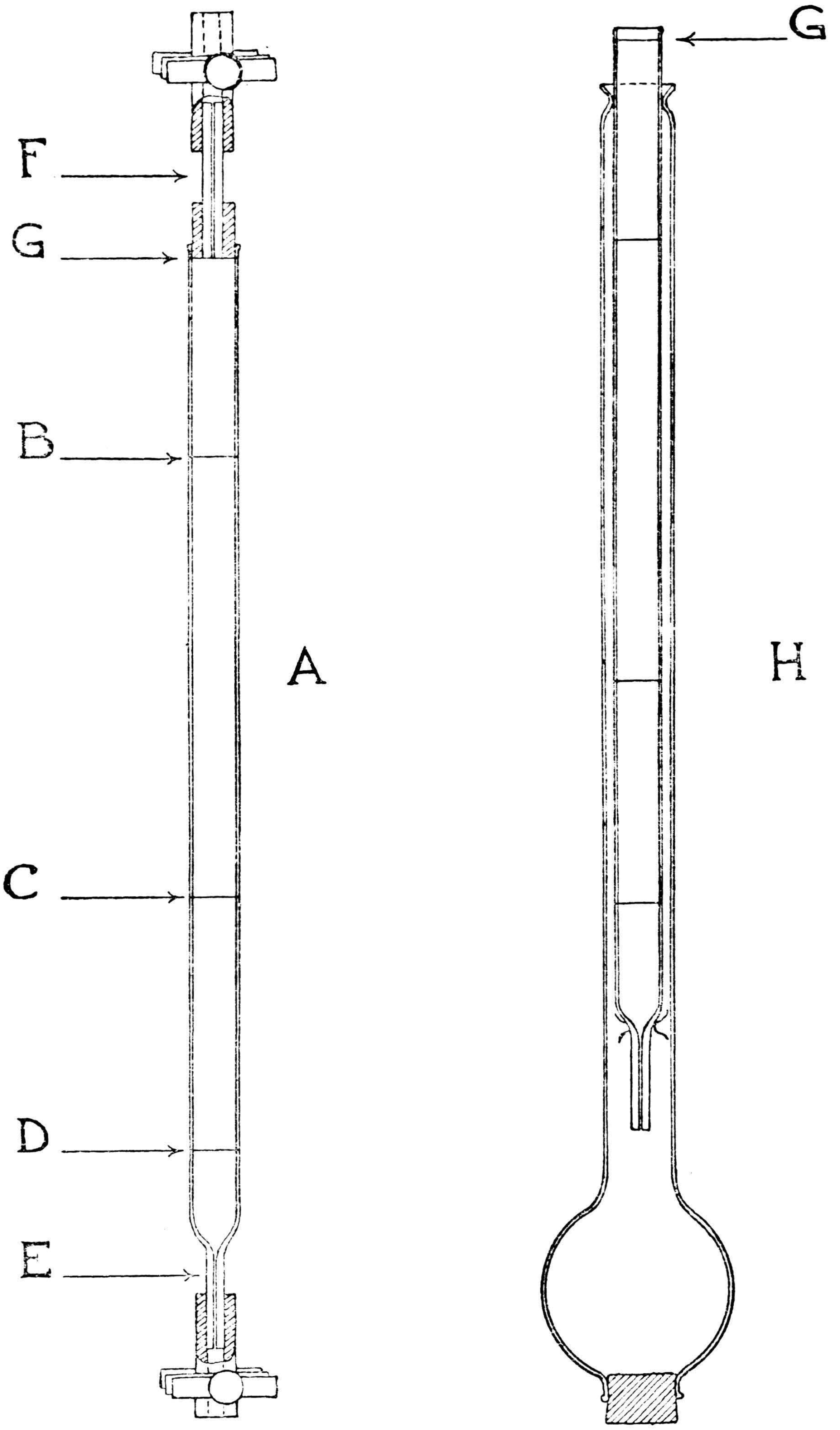

FIG. 1

of the capillary. The lower portion of the instrument consists of a short glass capillary E discharging the solution into air, and made from Jena KPG precision bore tubing. The instrument, when in use as a dissolution vessel, is closed at the lower end with rubber tubing and clip, and at the upper end with rubber stopper, glass capillary tube F, rubber tubing and clip; when the time of flow of the solution is being observed these closing devices are removed, and the instrument is supported in a glass jacket H immersed in a thermostat. The dimensions of the viscometer are as follows:—

Internal diameter of capillary E	0·088	±0·001	cm.
External diameter of capillary E	0·6	±0·2	cm.
Length of capillary E	2·5	±0·05	cm.
Internal diameter of wide tube A	1·0	±0·025	cm.
Wall thickness of tube A	0·1	to 0·15	cm.
Height of ring B above flat end of capillary E	24·2	±0·05	cm.
Height of ring C above flat end of capillary E	12·2	±0·05	cm.
Height of ring D above flat end of capillary E	6·2	±0·05	cm.
Distance of ring G below the top of tube A	about 0·4		cm.
Over-all length of instrument without closing devices	30·0	±0·2	cm.
Length of funnel-shaped seal between wide tube and capillary	about 1·0		cm.

The dimensions of the capillary F are unimportant.

The above specification is identical with that given in the report of the Fabrics Co-ordinating Research Committee[2] except in respect to the tolerance allowed on the capillary diameter, and the provision of the ring G. As a result of the use of precision bore tubing it has been possible to reduce the tolerance in capillary diameter to one half that previously allowed.

The method of using the viscometer only differs in the following respect from that described in the earlier paper: The steel stirrer is replaced by 0·7 cc. of mercury in order to avoid any risk of fracturing the glass at the capillary shoulder during the agitation of the viscometer contents by an end over end motion of the instrument; this volume of mercury was chosen to be equal to the volume of the steel cylinder previously used, so that the total volume of solution enclosed by the viscometer was unaltered by the change in the stirring device. The mercury is run in from a small burette after the capillary, and a portion of the wide tube, have been filled with the solvent, and before the addition of the cellulose. The mercury, broken up into small drops by the agitation, collects together at the bottom of the tube while the latter is standing in the thermostat immediately prior to observations of the rate of flow. It runs out with the first portion of solution, and is cleared from the viscometer before the surface of the solution reaches the first timing mark. The mercury is subsequently separated from the cuprammonium and set aside until sufficient has been collected, when it is washed, filtered, and used again.

(b) Calibration

The calibration of the viscometer includes the measurement of:

(1) The time of flow at 20° C. of a liquid of known fluidity and density, flowing sufficiently slowly to keep the kinetic energy correction low; from this the viscometer constant is calculated.

(2) The volume between the top and bottom timing marks B and D, from which is calculated the correction constant used in applying a kinetic energy correction to observations made on relatively fluid solutions.

(3) The total volume enclosed by the viscometer, used in calculating the weight of the cellulose sample necessary for obtaining a solution of the desired concentration.

Calibration with glycerol solution.—The method is substantially that described in the earlier paper. An aqueous solution is prepared containing 65% by weight of commercially pure glycerol, and its time of flow at 20° C. in the viscometer to be calibrated is measured. The kinematic fluidity (fluidity × density) of this solution at 20° C. is measured independently in a capillary U-tube viscometer of orthodox design. For convenience, the time of flow of the glycerol solution in the X-type viscometers is always reduced by calculation to that of a solution of kinematic fluidity 7·98 in c.g.s. units, the actual measured value never differing greatly from this figure. The time of flow of the calibrating solution in the X-type viscometers, when corrected in this way, is called the " Glycerol Calibration Time " and is used in calculating the instrumental constants as explained later.

Calibration with phenyl ethyl alcohol.—When, as in these laboratories, viscometers are calibrated in large numbers, the method just described appears as convenient as any, and is the one ordinarily used. For the occasional calibration of a few instruments it would evidently be advantageous if a standard reference liquid were available of reliably known fluidity that would avoid the necessity for a separate accurate measurement of the fluidity of the calibrating liquid. It seemed likely that among the high-boiling organic solvents now commercially available some would be found of sufficient purity, or sufficiently easily purified, to serve as standard reference liquids. After examination of the possibilities, benzyl alcohol and phenyl ethyl alcohol were chosen as offering prospects of good service in this connection. Fairly large samples were obtained (Messrs. Boake, Roberts & Co.) in a commercially pure state, and were re-distilled through a fractionating column. From the benzyl alcohol a main fraction, approximately 70% by volume, was taken boiling at 204·9° to 205·0° C. under the existing atmospheric pressure, and from the phenyl ethyl alcohol a fraction about 80% by volume, boiling at 219·3° to 219·8° C. The fluidities of the two purified alcohols were measured in U-tube viscometers made according to the specification of the British Engineering Standards Association[4], very small kinetic energy corrections being applied. That of benzyl alcohol was measured in viscometers of type 1, by comparison with water, and that of phenyl ethyl alcohol in type 2 viscometers by comparison with benzyl alcohol. The following results were obtained at 20° C. as the means of a number of closely agreeing observations in different instruments:

	Density, d at 20°C.	Fluidity, F at 20°C.	Kinematic fluidity, dF at 20°C.
Benzyl alcohol	1·0445	15·25	15·93
Phenyl ethyl alcohol	1·019	7·01	7·14

These measurements are based on a value of 99·5 for the fluidity of water at 20° C. The fluidity found above for phenyl ethyl alcohol is identical with that obtained by Bingham and De Turck[5] in a series of measurements covering a temperature range from 0° to 100° C.; the material examined by these authors was specially synthesised and purified by them. The fluidity of the commercially pure sample of phenyl ethyl alcohol only differed by 1 per cent. from that of the specimen purified by fractional distillation. The effect of hygroscopicity on its fluidity has been examined by allowing a small sample to stand in a shallow dish exposed to an atmosphere of 65 per cent. controlled relative humidity at the ordinary temperature. After three days, the fluidity of the sample had risen by 5 per cent. The fluidity of the main fraction obtained from the fractional distillation of the humidified sample was, within the experimental error, identical with that of the original unhumidified material. The hygroscopicity of phenyl ethyl alcohol is too small to affect its value as a standard reference liquid within the times, and under the conditions, of actual use for the purpose. On the other hand, a sample that has been stored for a long while, unless well sealed, should be dried or distilled before use.

The kinematic fluidity of phenyl ethyl alcohol is near that of the standard glycerol solution used for X-type viscometers, and its time of flow in these viscometers is therefore suitable for use as a calibrating measurement. It is suggested that for the calibration of individual instruments made to the specification it would be satisfactory to use a sample of commercially pure phenyl ethyl alcohol further purified by distillation, and to assume the value of 7·14 for its kinematic fluidity at 20° C.

The most recent measurement of the fluidity of benzyl alcohol found in the literature is 16·5 at 20° C., given by Sorkau[6] in 1914, and this is considerably higher than the value found above. If benzyl alcohol were used for the calibration of X-type viscometers a somewhat large (2·3 per cent.) kinetic energy correction would be involved. It provides, however, a useful secondary check.

The position of the middle timing mark.—The position of the middle ring C is calculated to be such that for normal viscous flow the time t_1 for the liquid surface to sink from B to C is equal to the time t_2 for it to sink from C to D; the ratio t_1/t_2 should thus be equal to unity. During the calibration of the viscometers with glycerol or phenyl ethyl alcohol time observations are made at the middle ring, and the ratio t_1/t_2 recorded.

The volume between the top and bottom timing marks.—This measurement is only required for the calculation of a correction, and need not therefore be made with the greatest accuracy. It is made by adding water to the instrument from a burette, and reading the volume of the addition necessary to raise the liquid level from the ring D to the ring B.

Total volume enclosed by the viscometer.—This is determined by weighing the viscometer and its closing devices, first empty, then filled with water in the same way as it is filled with cuprammonium for use. In order to calculate the weight of cellulose required to yield a solution of desired concentration the volume obtained in this way must be diminished by 0·7 cc.—the volume of the mercury stirrer.

(c) Calculation of Constants.

The fluidity, F, of a solution of density d is calculated from the equation:

$$dF = \frac{C}{t - K/t} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots (1)$$

where C is the viscometer constant, K the kinetic energy correction constant, and t the observed time of flow between rings B and D. The procedure for the calculation of the two constants is the following: The fluidity of the calibrating glycerol solution is such that the kinetic energy correction is very small, and the following relation is a close approximation:

$$dF = C/t_G = 7{\cdot}98$$

where t_G is now the Glycerol Calibration Time, and 7·98 is the kinematic fluidity of the standard glycerol solution. This gives the uncorrected viscometer constant C when the calibration time has been observed.

The value of the kinetic energy correction constant K is next calculated from the equation:

$$K = \frac{mV}{8\pi l} \times C$$

where V is the volume between the rings B and D, l is the capillary length, and m a factor to which is assigned the value 1·03. By the substitution of 2·5 for the capillary length in accordance with the specification of the instrument, and the uncorrected value $7{\cdot}98 t_G$ for C, the equation reduces to

$$K = 0{\cdot}131 t_G V$$

where t_G and V are the quantities directly observed in the calibration.

Finally, the value of K determined in this way is inserted in the equation (1) together with the Glycerol Calibration Time, and the kinematic fluidity of the standard glycerol solution. The equation can then be solved for C, the corrected viscometer constant, which differs by less than 1 per cent. from the approximate value used in calculating the correction constant.

When the viscometer is used for dilute cellulose solutions in cuprammonium, the density is regarded as constant and equal to that of the solvent, viz. 0·94 at 20° C. for a solvent of the standard composition given in Section 3. In this case it can be included in the constants of equation (1), thus

$$F = \frac{C/d}{t - K/t} = \frac{C'}{t - K/t} \quad \text{where } C = 0{\cdot}94\, C'$$

This is the form in which the equation is used in the routine measurement of fluidity.

The determination of the kinetic energy correction was discussed in the earlier paper[1], where it was pointed out that it could either be calculated from the dimensions of the instrument as above, or obtained experimentally from additional calibrating measurements with liquids of high and known fluidities (for example, water). There is some uncertainty as to the best value to use for the factor m that appears in the equation for the calculation of the kinetic energy correction from the dimensions of the instrument. The value used (1·03) was chosen because the mean values of the correction constant obtained from 100 X-type viscometers by the two methods were then identical.

(d) The Use of the Middle Timing Mark, and the Deviation of the Flow of Cellulose Solutions from the Poiseuille Law.

The fluidity of a solution is calculated from its observed time of flow t between the timing marks B and D, but in routine work a time observation is also made at the middle mark C, and the ratio t_1/t_2 recorded. This is the ratio of the times of flow in the two sections into which the mark C divides the volume BD, and should be equal to unity (within the limits allowed by the tolerances) for true viscous flow when the kinetic energy correction is small. At the lower end of the fluidity range, the value of t_1/t_2 will be less than unity for cotton solutions, on account of the departure of their properties from those of true viscous fluids, a subject already discussed in the earlier paper. As the fluidity rises, and the chemical degradation of the cellulose increases, the abnormality in flow properties diminishes, and the value of t_1/t_2 approaches unity. For 100 results taken at random from the records of routine measurements on 0·5 per cent. solutions of technically processed cotton materials, corresponding values of fluidity F, and time ratio t_1/t_2 were plotted. The points clustered round a smooth curve from which the values in Table I were read:

Table I

F	1·5	2·0	2·5	3·0	3·5	4·0	4·5	5·0	7·0	10·0	15·0	21·3
t_1/t_2	0·67	0·725	0·775	0·80	0·825	0·84	0·855	0·87	0·915	0·94	0·98	1·00

A gross divergence between the observed ratio t_1/t_2 and that to be expected from the above table shows that the capillary has become partially choked by obstruction with undissolved material during the flow of the liquid. In practice this only happens rarely, and then generally with samples of low fluidity that dissolve relatively slowly.

In the higher fluidity range the kinetic energy effect is considerable, and since it is different in the two sections of the viscometer BC and CD, the observed ratio t_1/t_2 again diverges from unity, becoming slightly greater than unity. From the dimensions specified for the instrument the times of flow of true viscous liquids of known kinematic fluidities in the two sections of the viscometer can be calculated with the aid of the Poiseuille equation including the kinetic energy term. If this is done the following values for the ratio t_1/t_2 are obtained:

Table II

dF	5	10	20	30	40
t_1/t_2, calculated for true viscous flow	1·002	1·008	1·036	1·067	1·083

These calculations were checked by observations in the X-type viscometers with commercial samples of benzyl alcohol and butyl phenyl acetate. At 20° C., their kinematic fluidities were 16·3 and 32·4 respectively, and the corresponding time ratios t_1/t_2 1·019 and 1·072. From the ratios recorded in Table I, it can be seen that the value for cotton solutions does not exceed unity until the kinematic fluidity reaches the neighbourhood of 20 ($F = 21·3$), though for true viscous flow it should be significantly greater at this fluidity as shown in Table II. Hence, even at a fluidity as high as 20, the flow of a cellulose solution still diverges slightly from the behaviour of a true viscous liquid.

The effect of increasing cellulose degradation on the deviation from the Poiseuille Law can be shown, not only by measurements of rate of flow made at a constant cellulose concentration, but also by observations of rate of flow under conditions that correspond to a constant fluidity, the concentration of the cellulose solution being varied to satisfy these conditions. Table III records data for six samples of the same cotton chemically degraded to progressively increasing extents; it contains the concentrations necessary to yield a solution of fluidity 5·4 and the corresponding time ratios t_1/t_2.

Table III

Fluidity, F	Concentration, gm. per 100 cc.	Time ratio t_1/t_2
5·4	0·312	0·76
5·4	0·50	0·90
5·4	0·75	0·96
5·4	1·45	0·99
5·4	1·85	0·99
5·4	2·80	0·99

Solutions of the stated concentrations all had the same time of flow in an X-type viscometer, but because their deviation from the Poiseuille Law varies as shown by the t_1/t_2 ratios, their times of flow, and the calculated fluidities, in some other type of viscometer would not necessarily be identical for the six solutions.

Table IV shows that, for the same cotton sample, the deviation from true viscous flow diminishes as the concentration of its solution is diminished.

Table IV

Concentration, gm. per 100 cc.	Fluidity F	Time ratio t_1/t_2
0·50	1·4	0·68
0·33	4·6	0·74
0·30	5·9	0·77
0·25	9·0	0·82
0·20	12·7	0·84

(e) Practical Reproducibility of the X-type Viscometer

The results obtained in the calibration of the first 200 X-type viscometers to be made have been collected and analysed. The instruments were made from glass tubing ordered from the makers to be within the diameter tolerances allowed by the foregoing specification. The diameter of the wide (1 cm.) tubing was checked before the instruments were made, but not that of the KPG capillary.

Calculated from the specification, and with the tolerances stated in the diameter of the wide tube and the position of the rings, the volume flowing between rings B and D is

14·13 cc., with a range from 13·36 to 14·90 cc.

The mean volume found for 200 instruments was

14·3 cc., with a range from 13·6 to 14·95 cc.,

the distribution being:

Interval	13·5/14·0	14·0/14·5	14·5/15·0 cc.
No. of instruments ...	19	144	37

The tolerance in the position of the rings allows a range of t_1/t_2 values from 0·985 to 1·015, and with all the 200 instruments the value actually lay between 0·98 and 1·01.

The Glycerol Calibration Time can be calculated from the dimensions of the instrument by Poiseuille's equation. If the values inserted in this equation are the calculated volume flowing (14·13 cc.), the logarithmic mean head (12·98 cm.) and the kinematic fluidity of the calibrating glycerol solution (7·98), the time of flow for a capillary of the specified dimensions is 238 seconds; very small kinetic energy and Couette corrections are included in this calculation. If, for the volume flowing, the actual mean value observed for the 200 instruments (14·3 cc.) is inserted in the equation, the calculated Glycerol Calibration Time is 241 seconds, and the range corresponding to the tolerances in capillary length, capillary diameter, and volume flowing, is 210 to 270 seconds.

The actual mean Glycerol Calibration Time for the 200 viscometers was 246·5 seconds, the range 226 to 268 seconds, and the distribution as follows:

Interval	220/230	230/240	240/250	250/260	260/270 secs.
No. of instruments ...	1	40	103	40	16

Of the 17 viscometers in the highest and lowest time intervals, 11—or about

65 per cent.—were also in the highest or lowest volume intervals, whilst only about 30 per cent. of the whole 200 viscometers were in the extreme volume intervals. The variability in the volume flowing—due to the tolerance on the diameter of the wide tube—is thus an important factor affecting the variability in the Glycerol Calibration Time. It can be calculated that the tolerance allowed by the specification in the diameter of the wide tube corresponds to a variation of about ±5·5 per cent. in the time of flow, whilst the tolerance in the diameter of the capillary corresponds to a slightly smaller variation in time of flow, namely, about ±4·5 per cent.

As a result of the use of KPG precision bore capillary, the reproducibility of the viscometer is no longer determined to a predominant extent by practical limitations to the uniformity in capillary diameter. The wide tube, of 1 cm. diameter, can only be obtained from the makers with a precision of ±0·025 cm., and then only by special arrangement; this causes a slightly greater variability in the time of flow than variations in the diameter of KPG capillary. The above analysis shows, however, that in practice the viscometers can be made without difficulty, to conform strictly with the specification.

The mean viscometer constant C for the 200 instruments was 1950 (or 2,075 for C') whilst the mean correction constant K was 465. The mean total volume enclosed by the viscometers when filled as for use was 20·3 cc. requiring 0·1015 gram of dry cellulose for a 0·5 per cent. solution.

3. CUPRAMMONIUM SOLVENT

The composition of the standard solvent now used in these laboratories is

15±0·1 grams of Copper per litre,
200±5 grams of Ammonia per litre,
and less than 0·5 gram of Nitrous Acid per litre.

This agrees with the recommendation of the Fabrics Co-ordinating Research Committee, but contains less ammonia than the solvent used by Clibbens and Geake (240 grams per litre).

The methods of preparation and analysis described by them are still in use, but the scale of the preparation has been greatly increased, and 50 litres of the standard solvent are now made in one batch in a small plant constructed of iron.

The density of the solvent specified above is 0·94 at 20° C., and its fluidity 72 in c.g.s. units at the same temperature.

4. SOME APPLICATIONS OF FLUIDITY MEASUREMENT

Systematic investigations of the chemically modified cottons made in these laboratories have shown the close relationship existing between the fluidity of a cotton solution and the important textile properties of the material, such as the tensile strength of the fibre. Chiefly as a result of these investigations, fluidity measurement is now widely used as a means for controlling the quality of finished cotton materials in so far as it is affected by the chemical attack of the cellulose in bleaching and other chemical processes. The measurement is also valuable for detecting and analysing the sources of damage in goods that are found to be defective in tensile, or other qualities, and a few methods of applying it for this purpose will be discussed.

(a) **The Presence of "Injurious Chemicals" in Cotton Goods, and the Standard Heat Test.**

When cotton goods that have been stored for some time are found to be below normal strength, the opinion is sometimes expressed that they contain chemical ingredients of an injurious nature—either residues of process liquors imperfectly washed out, or constituents of fillings, dyeings, etc. It is inferred that tensile weakening, or other textile depreciation, has occurred as a result of the slow action of such ingredients on the cellulose during storage. Specifications for cotton materials often contain clauses prohibiting the presence of such "injurious chemicals", usually without a statement of the means to be adopted for testing the conformity of a sample with the specified requirement.

Substances that might produce the postulated slow chemical modification of the cellulose are obviously those of an acidic nature, or those capable of developing acid, and the attempt is sometimes made to define what is to be regarded as the safe limits of acidity in cotton materials from this point of view. A more satisfactory test—because a more direct test—is to submit a sample to a standard high temperature in a closed vessel for a standard time, and to measure the resulting rise in the fluidity of the cotton. Any possible chemical attack of the cellulose by foreign materials is accelerated by the high temperature, and the heat treatment is thus equivalent to a prolonged storage test at the ordinary temperature, whilst fluidity measurement before and after the treatment affords the most general and accurate method of assessing its chemical effect on the cellulose.

The method used in these laboratories is to heat a sample weighing one gram or less for 18 hours at 110° C. in a small closed weighing bottle. Raw cotton, or efficiently bleached and washed cotton, generally suffers a rise of fluidity of only one or two units when submitted to this heat treatment. The result can be regarded as a satisfactory one provided that the rise in fluidity is less than three units since it will be shown below that cotton containing very small quantities of free mineral acid suffers greater rises than this when heated under the conditions specified. It will also be shown that certain salts used in cotton processing, particularly magnesium sulphate, also cause considerable rises of fluidity when cotton containing them is heated under the specified conditions. Whether or not these are to be considered as "injurious chemicals" depends upon the sense in which this term is used. Cotton containing magnesium sulphate, zinc chloride, etc., can be stored for very long periods at the ordinary temperature without appreciable chemical degradation of the cellulose, and in this sense the salts are to be regarded as non-injurious; if, on the other hand, the material is stored in a hot place, or receives some heat treatment in later processing, the presence of the salt may lead to abnormal chemical degradation of the cellulose. Whilst, therefore, a rise of fluidity of less than three units in the standard heat treatment affords satisfactory evidence of freedom of the material from injurious chemicals, rises greater than this can result from the presence of substances that may be, but are not necessarily, injurious.

Samples of a plain bleached cloth, and of the same cloth mercerised and bleached, were washed, first in dilute acid to remove possible traces of alkali, and then in distilled water until they were free from acid. The samples were air dried, and immersed in relatively large volumes of dilute sulphuric and hydrochloric acid solutions of different known concentrations. They were well impregnated, and excess liquid then expressed until the samples contained their own weight of the acid solution. Without further treatment, the samples were hung in the air to dry, and then subjected to the standard heat treatment. Finally, they were washed, dried, and cut up into small fragments, which were mixed and sampled for fluidity measurement. The fluidities of the material after heating with and without acid are given in Table V for acid solutions of different fractional normalities. The original fluidities of the samples before heating were 4·5 for the plain bleached, and 6·1 for the mercerised bleached cloth.

The table shows that even with mineral acid solutions as dilute as *N*/1,000 —corresponding to a weight of actual acid on the cloth below 0·005 per cent.— the rise in fluidity on heating is considerably greater than 3 units.

Experiments similar to those recorded above were made with the plain bleached cloth impregnated with the five organic acids butyric, acetic, lactic, citric and tartaric in the two concentrations *N*/100 and *N*/10, the fluidity of the cloth after the standard heat treatment being given in Table VI.

Table V

Concentration of impregnating acid	Fluidity of cloth after heating			
	Plain bleached cloth impregnated with		Mercerised bleached cloth impregnated with	
	H_2SO_4	HCl	H_2SO_4	HCl
Nil	5·5		7·5	
N/1000	10·4	16·6	12·1	23·6
N/500	13·2	28·1	13·7	—
N/250	40·4	45·8	32·8	36·3
N/100	42·2	45·0	46·1	48·3

Table VI

Nature of acid	Fluidity of heated cloth impregnated with acid solution of concentration		Dissociation constant of acid
	N/100	*N*/10	
None	4·9		—
Butyric ..	7·3	6·2	$1·5 \times 10^{-5}$
Acetic ..	7·2	8·9	$1·8 \times 10^{-5}$
Lactic ..	9·1	20·1	$1·4 \times 10^{-4}$
Citric	13·0	22·4	8×10^{-4}
Tartaric ..	14·3	30·1	$9·6 \times 10^{-4}$
Sulphuric ..	42·2	—	Strong acid
Hydrochloric..	45·0	—	Strong acid

The values for *N*/100 sulphuric and hydrochloric acids in Table VI are included for comparison, and are taken from Table V. The results illustrate the much milder cellulose-modifying effect of the weaker organic acids, and show that the effect is related to the strength of the acid as measured by its dissociation constant. The requirement that the rise of fluidity in the standard heat treatment should be below three units would exclude lactic, citric, and tartaric acids in concentrations down to *N*/100 and below, but would not exclude acetic and butyric acids except in considerable concentrations.

Large rises of fluidity, presumably caused by acid attack of the cellulose, occur on heating cotton containing salts of the less basic metals and the strong mineral acids. Table VII records the fluidities of samples of the plain bleached cloth filled with 1 per cent. and 5 per cent. of the sulphates of sodium, magnesium, ammonium and aluminium on the weight of the cotton after the material had been submitted to the standard heat treatment, and the salts subsequently removed by washing with water. The percentage weights of the sulphates are expressed in terms of the anhydrous salts.

Table VII

Salt	Fluidity of cloth heated with sulphates	
	1% by weight	5% by weight
None	5·2	
Sodium sulphate ..	5·8	5·5
Magnesium sulphate	8·4	13·0
Ammonium sulphate	12·2	19·1
Aluminium sulphate	40·5	42·0

The effect of sodium sulphate is insignificant, of magnesium and ammonium sulphates definite, and of aluminium sulphate very great. As is to be expected from the above result, the presence of an Epsom Salt filling in finished cloth causes it to suffer a considerable rise of fluidity in the standard heat treatment—frequently from ten to fifteen units—and this is not due to the presence of magnesium chloride as an impurity in the filling. In agreement with these observations, cloth filled with Epsom Salt is more liable to damage by ironing, or hot pressing, than pure bleached, or bleached and dyed, material. The filling of certain cloths with Epsom Salt is a well-established finishing practice, and it is not to be inferred that the rise in fluidity on heating such materials necessarily places the salt in the category of " injurious chemicals " within the trade meaning of the term. Under ordinary conditions of storage, the filled material suffers no sensible deterioration within long periods, but a general appreciation of its greater sensitiveness to dry heat treatments of all kinds is desirable.

The heat test can be applied to cotton in its unbleached condition, or to cloth in its loom state. Since, however, unpurified cottons, or materials containing size ingredients, do not dissolve completely in cuprammonium, some process of purification is necessary before fluidity measurement. The standard method used in these laboratories is to boil unbleached cotton for one hour with a large excess of a 1 per cent. sodium hydroxide solution, subsequently to wash it in water, and to dry it in the air. In the case of loom-state cloth, the bulk of the size is first removed by thorough washing in hot water before the alkaline boil specified above. The comparison is then made between the fluidities of the cotton (a) purified in this way and not otherwise treated and (b) submitted first to the standard heat treatment, then purified as described.

The well-known effect of the alkaline earth chlorides, when used as size ingredients, in reducing the stability of cotton materials towards heat treatments can be readily shown. A number of cloths were available in loom-state, made from the same yarns, of the same construction, and all with warps containing 30 per cent. of size. In some of these the size was a pure starch and tallow mixture, whilst others contained in addition various amounts of calcium, magnesium and zinc chlorides as sizing ingredients, this being the only difference between them. Table VIII records the fluidities of these materials before and after the standard heat treatment, it being understood that all samples, whether heated or not, were boiled with alkali before the fluidity measurement. The chloride contents are expressed as percentages of the anhydrous salts on the weight of the loom-state cloth.

Table VIII

Fluidities of Cloths, free from or containing Chlorides, before and after Heating

Samples free from chlorides :—

Unheated	3·2	3·6	2·9	3·2	Mean 3·2
Heated	4·9	5·8	5·0	5·2	„ 5·3

Samples containing chlorides :—

Amount of chloride	Zinc chloride		Magnesium chloride		Calcium chloride	
	Unheated	Heated	Unheated	Heated	Unheated	Heated
0·85% ..	3·3	9·3	3·0	8·3	3·9	9·0
1·4 % ..	3·8	14·0	2·8	13·4	4·3	9·0
2·3 % ..	4·2	17·5	3·1	21·7	4·4	16·0

The presence of zinc, magnesium or calcium chloride is seen to cause increased degradation of the cellulose in a standard heat treatment when the results for the chloride-containing materials are compared with those for the loom-state cloth without these chlorides, and the effect increases with increasing salt content. The experiments described were made eight years after the cloth had been woven, and the fluidities of the unheated cloths show that the effect of the chlorides on the cellulose is negligible under ordinary conditions of cloth storage.

For comparison with the cloths containing zinc chloride, cloths were also available containing the acetate of this metal, instead of the chloride, but otherwise identical. Samples of these containing 2·3 per cent. and 3·7 per cent of zinc acetate showed no greater rise of fluidity in the standard heat treatment than the cloths containing nothing but starch and tallow as size ingredients.

(b) Differentiation between Chemical Attack occurring in Piece Finishing and that occurring in Laundering.

When tensile weakening of made-up cotton articles such as shirts, sheets, etc., has been proved by fluidity measurement to be due to chemical attack of the cellulose it is sometimes necessary to decide whether the attack resulted from the piece finishing treatment, or from laundry treatment of the made-up goods. Direct evidence on this question is often impossible to obtain, but reliable indirect evidence can be obtained when the articles contain cotton materials of different origin from the shirting, sheeting, or dress cloth primarily in question. Collars, cuffs or other parts of the articles frequently contain, for example, cotton linings of entirely different construction and origin from the principal cloth. If the cotton composing both the lining and the garment itself is characterised by high fluidity, the inference is justified that the chemical attack occurred after the goods were made up, whilst a high fluidity in the garment combined with a low fluidity in the lining points to the piece treatment as the source of damage. The more " subsidiary cotton parts " that can be tested in this way, the more irrefutable becomes the conclusion, and both maker's or retailer's tabs and the sewing thread in hems, etc., can usefully be examined for this purpose. The sewing thread is often the only available " subsidiary cotton part " available, but a large fluidity difference between a sewing thread and the fabric in the immediate neighbourhood of the stitches is satisfactory evidence that laundry treatment is not responsible for the higher fluidity. The total weight of sewing thread available for such investigations is often small, and the need then arises for a method of fluidity measurement requiring a much smaller sample than the standard capillary type viscometer.

(c) Very Localised Chemical Attack.

The same need arises in another kind of diagnostic investigation, namely, the examination of fabrics containing actual holes suspected of being caused by splashes or drops of acid, or other cellulose-degrading chemical. The attack is then exceedingly local, most of the attacked cotton has disintegrated and disappeared, and the only parts likely to yield evidence of the chemical damage are the extreme fringes of the holes. A sample of the minimum weight is desirable since the deeper the fringe cut from round the holes the greater is the dilution of the chemically attacked cotton with the chemically sound cotton, and the less conclusive is the result of the fluidity measurement. Very local attack, such as that caused by a spray of acid, when it has not resulted in actual holes, can often be detected by dyeing the cloth, for example, with a basic colour such as Methylene Blue. The presence of small spots of relatively dark shade in the basic dyeing affords provisional evidence of chemical attack, final proof being obtained by comparing the fluidity of the darker dyed parts with that of the lighter. A preliminary dyeing of the cloth is sometimes advisable when actual holes are present in order to decide what depth of fringe can safely be cut.

For cases of the kind described above, where only small samples of cotton are available, a type of rolling sphere viscometer has been designed, and has proved of great service during several years of use in these laboratories. The weight of the cotton sample required for fluidity measurement in the rolling sphere viscometer is about 0·01 gram, or one tenth that required for the standard capillary type viscometer.

5. THE B.C.I.R.A. ROLLING SPHERE VISCOMETER

(a) Specification and Method of Use.

The instrument is illustrated in Fig. 2. It consists of a glass tube 180 mm. long made from KPG precision bore tubing of internal diameter 3·60 ± 0·01 mm. The tube is closed at the two ends by ground glass stoppers A and B, one of which (A) is perforated by a fine capillary opening. The stoppers are held in position by rubber bands fitting over projections, and three rings are etched on the tube at distances of 15, 90 and 165 mm. from the upper end A. A cylindrical silver weight (C), 10 mm. long by 1·5 mm. in diameter, is used for stirring the cotton solution.

As in the standard method, the dissolution of the cotton takes place in the viscometer itself. The material is cut very fine, and a sample taken of such a weight that when dissolved in the volume of cuprammonium required to fill the viscometer the concentration of the resulting solution is 0·5 gram of dry cotton per 100 cc. (0·5 per cent.). For unmercerised materials, it is sufficiently accurate to assume a moisture content of 6 per cent., but the weighing should be accurate to 0·1 milligram since the total quantity weighed is only of the order of a few milligrams. The weight of cotton required for each viscometer after allowing for this moisture correction is conveniently recorded as a calibration constant of the instrument. The filling of the

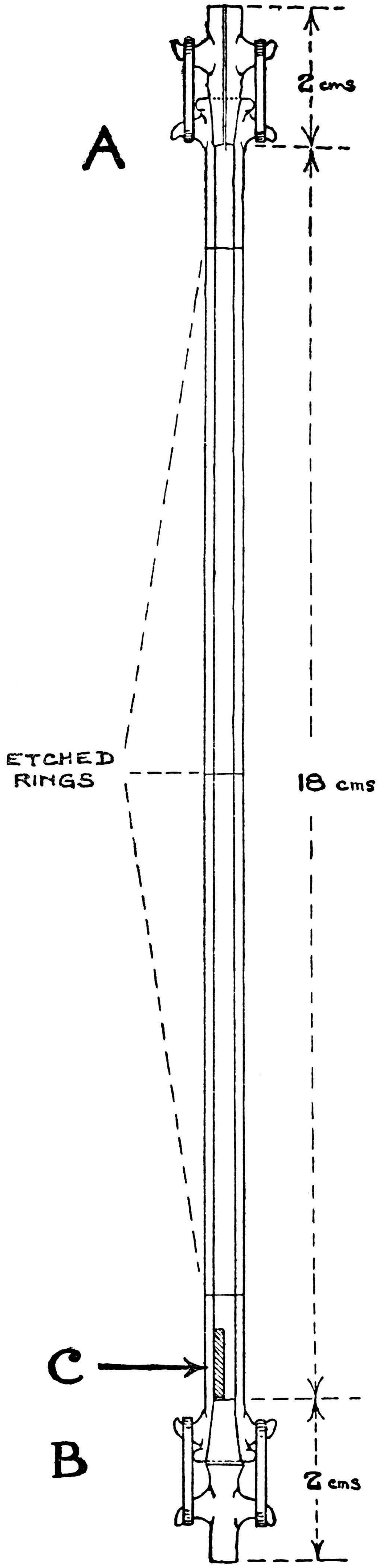

FIG. 2

viscometer is done with the instrument in an upright position, the stopper A being removed and the stopper B in place. The sample of cotton is weighed directly into a small funnel made from thin glass tubing, which is then placed in the top of the viscometer, already partly filled with cuprammonium. By means of an iron or nickel wire the cotton is transferred to the viscometer, mixed rapidly with the cuprammonium, and the instrument then completely filled with the solvent. In order to fill the narrow viscometer conveniently it is necessary to provide the solvent reservoir with a fine glass outflow jet. The stopper A is inserted and the excess cuprammonium is forced out through the capillary, which can then be sealed with a small piece of soft wax. A homogeneous solution is obtained by fastening the viscometer to a slowly revolving wheel so that it receives an end over end motion, and the silver weight travels continuously from one end of the tube to the other and back again with each revolution of the wheel; at least for the more viscous solutions, this stirring is continued overnight, and the solution is meanwhile protected from light by wrapping the instrument in a black cloth.

After removal from the wheel, the viscometer is allowed to stand in an upright position for 15 minutes, and a steel sphere 1/32-inch in diameter is then inserted, for which purpose the stopper A is momentarily removed and replaced. The spheres consist of standard Hofmann ball bearings of the specified diameter. The time taken for the sphere to roll down the inner surface of the tube from the top to the bottom timing ring is then determined when the viscometer is held accurately at an angle of 20° to the horizontal. A special frame, described later, is used to hold the instrument in the correct position, both frame and viscometer being immersed in a thermostat at 20° C. during, and for 15 minutes prior to, the timing. The steel ball is brought from the lower end B to the higher end A by means of a magnet, and its time of roll between the top and bottom rings is noted with a stop watch, the viscometer and its contents being illuminated by a lamp immediately behind the glass-sided thermostat. Ten observations are made with the same sphere, and the average time of roll is used in calculating the fluidity of the solution. Between each of the ten successive observations the viscometer is twisted through about 90° so that the path of the rolling sphere follows different lines on the internal surface of the viscometer tube. The time of the passage of the sphere past the middle ring is also observed as a check on the homogeneity of the liquid; if the average time of roll from the upper to the middle ring is considerably different from the average time between the middle and the lower ring, the stirring must be continued until the two are equal within the limits of observational errors.

The frame used for holding the instrument at the correct angle during the rolling of the sphere is illustrated in Fig. 3. It consists of a brass casting XYZ in the form of a right-angled triangle, of which the long side YZ forms an angle of approximately 20° with the horizontal side XY. The long side carries two V-grooved blocks A and B, and during the measurement the viscometer lies in these, and is held in position by springs such as that shown at C. The stand is supported in the water thermostat by means of a separate metal rod E clamped at its lower end in the block D, and at its upper end to a retort stand or other carrying device. The sides of the frame are provided with two lugs through which pass the setting screws F and G, and the frame is so adjusted in the thermostat that the pointed tips of these screws are both accurately on the water surface. This precisely defines the position of the frame to the extent of ensuring that a straight tube lying in the V-blocks is inclined at an angle of 20° to the horizontal. The adjustment of the screws F and G to satisfy this condition is made once and for all by means of an accurately made jig, and the screws are locked in position by means of lock nuts.

(b) Calibration

The calibration data include the volume enclosed by the viscometer, and the time of roll of the sphere in a liquid, or liquids, of known fluidity and density. The volume of the instrument is determined by weighing it empty, and filled with water at 20° C., the silver stirrer being in position. The volume calculated from the specified dimensions is 1·815 cc. and the corresponding weight of cotton required for a 0·5 per cent. solution is 0·00907 gram dry, or 0·00965 at 6 per cent. moisture content.

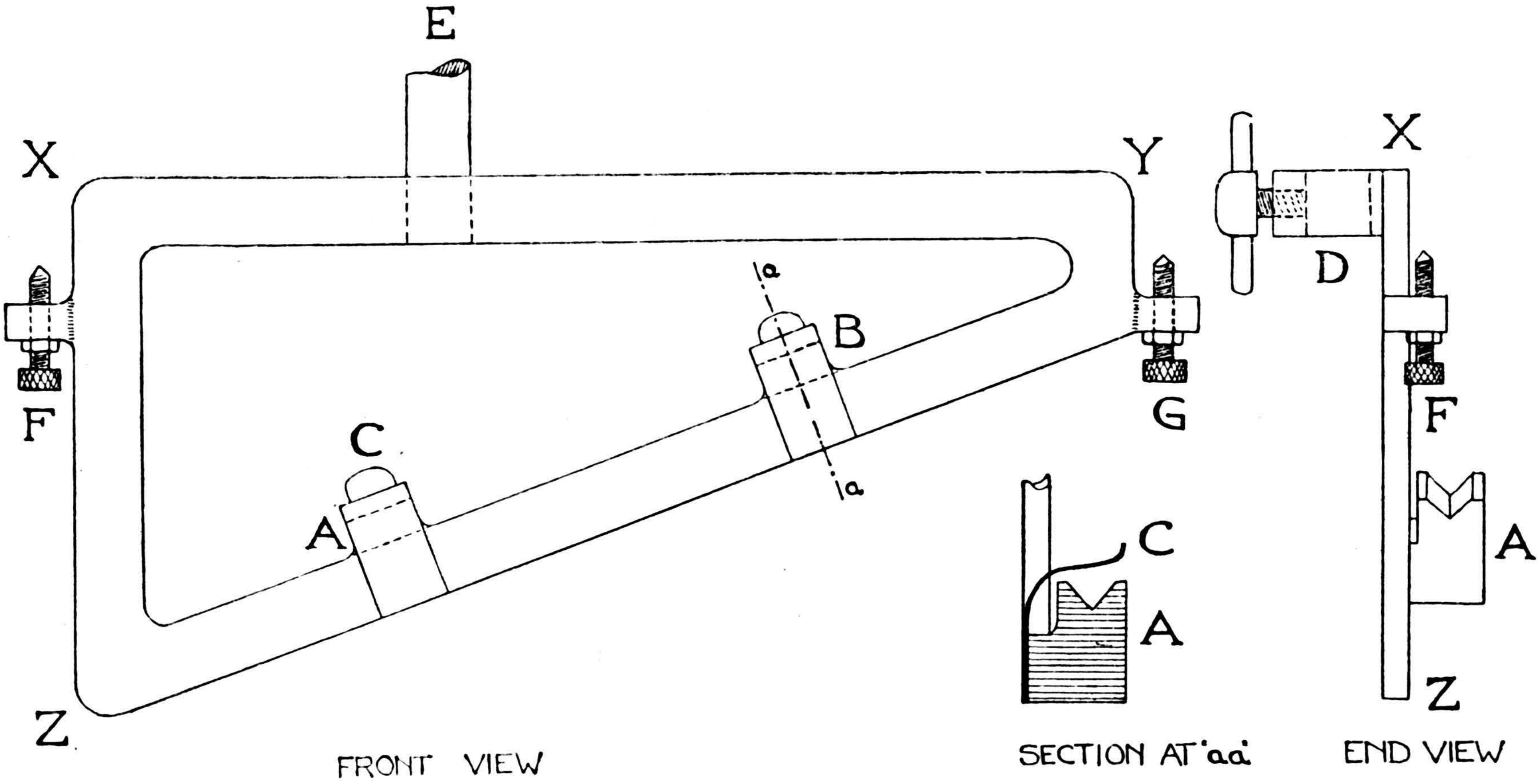

FIG. 3

As a standard reference liquid, pure phenyl ethyl alcohol is used. The viscometer is filled with the liquid, and the time of roll of the sphere at 20° C. from the top to the bottom timing mark is determined as the mean of a number of observations with the same sphere, as already described for cotton solutions; the value obtained is checked by similar observations with a second sphere.

(c) Calculation of Fluidity from Instrumental Constants

The conditions of liquid flow in the rolling sphere viscometer are not capable of theoretical treatment (cf. Barr[7]), but when the results obtained with a number of liquids are examined they are found to be represented within certain limits by the formula

$$F = K_0/t(D-d)$$

where F is the fluidity of the liquid, t the time of roll, D and d the densities of the sphere and the liquid respectively, and K_0 a constant. This is an equation of the same form as applies in the case of the falling sphere viscometer. The density of the steel sphere can be taken as 7·6, the density of phenyl ethyl alcohol is 1·019, and its fluidity 7·01 at 20° C. If these values and the time of roll in phenyl ethyl alcohol, are inserted in the equation, the constant K_0 can be calculated. For 0·5 per cent. solutions of cotton in cuprammonium, the density of the liquid is 0·94, the value of $D-d$ for steel spheres is then 6·66, and the equation can be written in the form

$$F = K_o/6{\cdot}66t = K_1/t, \text{ where } K_1 = K_o/6{\cdot}66$$

This is the simple relation used in the routine calculation of fluidity from observations in the rolling sphere viscometer, the constant K_1 being calculated and recorded for each viscometer.

(d) Examination of the Validity and Limitations of the Method

The calculations of the previous paragraphs are based upon an empirical equation of restricted applicability, and the measurements described below were carried out with the object of checking the accuracy of the method.

Observations with several true viscous liquids.—The times of roll of the sphere under the conditions described have been determined in three viscometers made to the specification and filled with commercial samples of glyceryl triacetate, phenyl ethyl alcohol, benzyl alcohol and butyl phenyl acetate. The results are given in Table IX, together with the fluidities and densities of the samples at 20° C. measured independently by orthodox methods.

Table IX

Liquid	Density at 20°C.	Fluidity at 20° C.	Time of roll (seconds) in viscometer		
			No. 16	No. 17	No. 18
Glyceryl triacetate	1·159	4·47	39·2	39·2	39·3
Phenyl ethyl alcohol ..	1·019	7·14	23·6	23·9	24·1
Benzyl alcohol	1·045	15·55	11·5	11·6	11·3
Butyl phenyl acetate ..	0·992	31·0	5·8	—	—

The product $tF(D-d)$, equal to the constant K_o, has been calculated from each separate observation, and is given in Table X. The results show that over the fluidity range 4 to 31 the product is approximately constant, though there is a tendency for its value to increase with rising fluidity, that is, with diminishing time of roll of the sphere.

Table X

Fluidity of liquid	Product $tF(D - d) = K_o$		
	Viscometer 16	Viscometer 17	Viscometer 18
4·47	1130	1130	1130
7·14	1110	1120	1120
15·55	1170	1180	1160
31·0	1190	—	—

The observed times of roll are fairly short, namely, from about 35 to 4 seconds for the fluidity range of 5 to 40, compared with times of flow of 400 to 60 seconds in the standard capillary viscometer for the same fluidity range. The time of roll corresponding to a given fluidity can be increased by diminishing the angle at which the viscometer is tilted to the horizontal, being approximately inversely proportional to the sine of that angle. Although a slightly smaller angle than 20° could probably be used, a limit exists beyond which the disturbing effect of very slight irregularities on the glass surface becomes apparent.

Comparison of results obtained on cotton solutions in the rolling sphere viscometer with those obtained in the X-type capillary viscometer.—A more direct check on the method is obtained by measuring the fluidity of the same cotton solution in both the rolling sphere, and the X-type capillary viscometer.

In order to do this, 0·5 per cent. solutions of different cottons were prepared in the usual way in X-type viscometers, and rolling sphere viscometers were filled directly from them by connecting the capillary tubes of the former with the perforated stoppers of the latter. The volumes necessary to fill the rolling sphere viscometers were so small that sufficient solution remained in the X-type viscometers to permit the observation of the times of flow in the usual way. Table XI provides a comparison of the results obtained with the two types of instrument. The constant obtained by calibration with phenyl ethyl alcohol was used for calculating fluidity from observations in the rolling sphere viscometers.

Table XI

Rolling Sphere Viscometer No. 17

Fluidity from X-type viscometer	5·1	6·8	9·6	11·0	15·1	20·8	27·5
Fluidity from rolling sphere viscometer ..	5·0	6·4	9·2	10·5	13·9	19·4	25·7
Difference	0·1	0·4	0·4	0·5	1·2	1·4	1·8

Rolling Sphere Viscometer No. 18

Fluidity from X-type viscometer	5·0	7·4	9·2	10·9	14·6	20·1	27·1
Fluidity from rolling sphere viscometer ..	5·1	7·4	8·9	10·5	13·9	18·5	24·9
Difference	—0·1	0·0	0·3	0·4	0·7	1·6	2·2

The comparison shows fair agreement between the two methods, but there is a significant discrepancy increasing as the fluidity rises. This is merely another expression of the fact that the " constant " in the equation used to calculate fluidity from observations in the rolling sphere viscometer is not strictly constant, but shows an upward drift as the time of roll diminishes. By the introduction of another empirical constant into the equation it is possible to bring the fluidity results calculated from observations in the rolling sphere viscometer into substantial agreement with those yielded by the standard capillary method over the whole fluidity range of interest. For the purpose of the comparative measurements which the rolling sphere viscometer is alone intended to provide, any considerable absolute accuracy, even if it were obtainable, would, however, be purposeless. The instrument is used for diagnostic work of the kind described in Section 3, for example, to determine whether there is a large or only a small fluidity difference between a sewing thread and the fabric into which it is sewn, or between the fringes of a hole and the surrounding material.

The rolling sphere viscometer would not be used for systematic investigations, nor for any purpose for which the standard capillary method could be used, but it yields good service in detecting large fluidity differences between small samples, and the method using the simple formula with one calibration constant is sufficiently accurate to provide the information required of it in practice.

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29—THE GEOMETRICAL BASIS OF PATTERN DESIGN

Part IV*: Counterchange Symmetry in Plane Patterns

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INTRODUCTION

In Part III plane patterns were considered from the point of view of geometrical symmetry alone; the only symmetry operations allowed were movements of various kinds, and subject to this restriction it was found that there were only 17 types of pattern. The next step is to extend the analysis to the field of counterchange patterns, as has already been done in Part I for borders.

It will be remembered that there a new symmetry operation—reversal—was introduced, the operation consisting of an interchange of black and white, and that other hybrid operations were evolved from geometrical movements and reversal in terms of which the border types were described. These operations were:—rotation about a *centre of reversion* of even order, followed by a reversal; rotation about an *axis of reversion* followed by a reversal; a screw about a *screw-reversion axis* followed by a reversal; and a *reversion-translation* in which a translation was followed by a reversal. In borders this last was restricted by the fact that the translations of the pattern were all in one direction (along the border); in plane patterns we have to deal with reversion-translations in which the translational part of the operation may be in any direction in which the pattern has translations; if t is the least translation in any such direction, then a possible reversion-translation consists of a translation $\frac{1}{2}t$ in this direction followed by a reversal.

These operations, consisting of reversal together with a geometrical movement, may be called "counterchange operations." A pattern is then a "counterchange pattern" when it may be superposed on itself by a counterchange operation.

TYPE-SYMBOLS

For the concise description of the counterchange types we proceed as in borders, introducing such modifications as are necessary. Centres of reversion of the second, fourth and sixth orders are denoted by $2'$, $4'$, and $6'$ respectively; reversion and screw-reversion axes are represented by $2'$ and $2'_1$ in the second or third place in the symbol. With regard to reversion-translations we keep a, as in borders, to stand for one parallel to the side a of the cell and we use b for one parallel to the other side of the cell. It is not difficult to show that when a pattern has a reversion-translation in *any* direction there must be one also either in one of these directions or else along a diagonal of the cell, however the unit cell is chosen (Appendix (ii)). When there is one in this third direction it is represented by n in the type-symbol. As in borders, the symbol for a reversion-translation takes the place of that for the central symmetry, unless the latter has to be shown to eliminate any ambiguity (there are a few exceptional cases where the central symmetry is not implied in the following terms giving the axial or screw symmetry). When this is the case, the type-symbol will contain terms like $2/a$ (centres

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*Parts I, II and III, appeared in this *Journal*, 1935, **26**, T197; T293; T341.

of the 2nd order and reversion-translations parallel to *a*) or 4/*n* (centres of the 4th order and reversion-translations parallel to a diagonal of the cell).

The type-symbols, then, are to be read as follows :—the first term will always show the reversion-translations, if there are any, but it *may not* show the central symmetry (thus *a* does not deny central symmetry, but 2 or 4 or 6 denotes central symmetry *without reversion-translations*). The second and third terms are used to denote the presence or absence of axes (a 1 in either of these places shows a lack of axes of any kind in a certain direction). Axes are shown according to the order of precedence :—symmetry axes, screw axes, reversion axes, screw-reversion axes. Thus 2 in the second or third place of the symbol implies pure axial symmetry without denying screw, reversion, or screw-reversion axes in the same direction ; 2_1 only occurs when there is no symmetry axis parallel to the screw axis, and it implies nothing whatsoever about the existence or otherwise of reversion or screw-reversion axes in the same direction ; and so on for the others—a screw-reversion axis is only shown when there are none of any of the others parallel to it.

The only other point needing emphasis is the fact that in the symbols used the order of the terms is of the utmost importance. To fix our ideas we shall, as usual, draw one side of the cell horizontal, and we shall call this side *a* and the other *b*. Then the second term of the symbol always refers to axes parallel to *a*, and the last term to axes parallel to *b* (except that in square or hexagonal patterns it refers to secondary axes, the convention as to primary and secondary remaining as in the fundamental types). Thus *a*21 and *a*12 are quite different types, for the former has symmetry axes parallel to the reversion-translation and the latter has them at right-angles to it ; but *a*21 is the same type as *b*12, and *a*12 is the same as *b*21.

As in the fundamental pattern types the whole symbol is prefixed with a *c* when the net of the pattern is centred-rectangular.

SYMMETRY DIAGRAMS

Many of the types of counterchange symmetry are too complicated to be described without the help of diagrams of the kind used in Part III ; those given here need a few words of explanation in order that they should be understood. We have already given, in Part I, the types of point-symmetry which can occur in counterchange patterns, and it was also pointed out there how a counterchange operation could be illustrated by the use of " positive " and " negative " arrows which end in a dot or a circle.

When a pattern has a purely geometrical symmetry element these arrows are arranged so that the symmetry operation superposes every arrow on one of the same sort. The geometrical part of a counterchange operation, however, interchanges the positions of the positive and negative arrows, so that the operation of reversal means that each positive arrow must be made negative and *vice-versa*. The positions of geometrical symmetry elements are shown in the same way as in Part III ; 2-, 4-, and 6-fold reversion centres are denoted by crosses, black-and-white squares, and black-and-white hexagons respectively ; a reversion axis is shown by a black elliptical figure at one end of the line (which is dotted if it is also a screw axis) ; and a screw-reversion axis is marked by the symbol ʔ at one end. Reversion-translations are never shown in the diagrams, as their existence is always obvious.

THE TYPES OF COUNTERCHANGE SYMMETRY

The way in which we set out to discuss the problem now before us is a generalisation of that used for the counterchange borders. These were obtained from the fundamental types by adding reversals to certain of the symmetry operations; this is the simplest procedure so long as we are only concerned with the description of the new types. An alternative method would be to introduce certain point-symmetries into the unit cell, as was done for the fundamental types in Part III, and this is the better procedure when a more rigorous demonstration that the types obtained are the only ones possible is desired. For our present purposes, however, the added complication is undesirable, and we shall use the simpler method.

We start by taking any one of the fundamental types (the *basic* pattern) as represented diagrammatically in Part III, and we search for counterchange *derivatives* by adding reversals to certain of the symmetry operations. In effect, this means that we change half the arrows in the diagram of the basic type from positive to negative, and each different way in which this can be done gives a possible counterchange derivative. The relation between a basic type and its derivatives is then quite simple. If one of the diagrams of Figs. 1-3 is taken, and the reversion elements replaced by the corresponding pure symmetry elements—a process which removes the distinction between positive and negative arrows—then the resultant diagram is one of the 17 which were given in Part III, except that it may be of greater extent (contain more than one cell) when the counterchange pattern has reversion-translations.

That a relation of this sort must exist between any counterchange type and one of the fundamental types is shown in the Appendix. Once it is granted that this is so, the derivation of the counterchange types is reduced to a kind of geometrical parlour game:—given one of the diagrams of Part III, extended to show a number of cells instead of just one, in how many ways can we make half the arrows negative whilst satisfying the conditions (*a*) a movement taking any arrow to the position originally occupied by one of the same kind interchanges all the positive arrows amongst themselves and all the negative ones amongst themselves; (*b*) a movement taking any arrow to the initial position of one of the other kind interchanges all the positive with all the negative arrows?

Derived from Type 1. There is only one derivative of this type. It is obtained by taking a basic pattern with translations $\frac{1}{2}a$ and b; two cells of this make up a new cell of sides a and b, which is the cell of the counterchange pattern. One half of this is made the negative of the other in order to give the counterchange type $a11$. The characteristic of this type is that it has only reversion-translations as symmetry elements (other than ordinary translations); if instead of being parallel to a they are parallel to b the type is $b11$. Another way of deriving the type is to introduce reversion-translations along both sides of the unit cell of the basic pattern (in this case the cell must be of the dimensions $\frac{1}{2}a \times \frac{1}{2}b$); then the counterchange pattern will have translations along the diagonals of the basic cell. Diagram 1 (Fig. 1) shows the unit cell of $a11$.

Derived from Type 2. The diagram of the unit cell of a pattern of this type contains only centres of symmetry of the second order. If all of these are changed to reversion centres we obtain the type $2'11$, of which Diagram 2 shows the unit cell. Pattern No. 2 is an example of this type.

Taking a basic pattern of the type 2 with translations $\frac{1}{2}a$ and *b*, we can obtain a pattern having a reversion-translation parallel to *a*, that is, of the type 2/*a*11. Alternate *b*-chains of symmetry centres have been changed into reversion centres, as shown in Diagram 3. The alternative 2/*b*11 is illustrated in Pattern No. 3.

Derived from Type 12 *or* 112. In a pattern of the type 112 (translations *a* and *b*) there are symmetry axes parallel to *b* at intervals $\frac{1}{2}a$. Changing them all into reversion axes leads to the type 112′ (Diagram 4); when the axes are parallel to *a* we write 12′1, of which Pattern No. 4 is an example. If in a pattern of the type 112 (translations $\frac{1}{2}a$ and *b*) we change every alternate axis into a reversion axis we get the type *a*12. Diagram 5 shows how the reversion-translation arises, and Pattern No. 5 is an example of this type. When the axes are parallel to *a* the type-symbol is *b*21.

Starting with a basic pattern, whose translations are *a* and $\frac{1}{2}b$, of the type 112, we derive the type $b12_1$ by making every axis a reversion element and introducing a reversion-translation parallel to *b*. The reversion axes then become screw axes as well, as may be seen in Diagram 6. Pattern No. 6 is of the type $b12_1$; the other orientation is $a2_11$. Using the same basic pattern, but retaining the symmetry axes, the introduction of a reversion-translation parallel to *b* gives the type *b*12. Here each axis is also a screw-reversion axis (Diagram 7). Pattern No. 7 is evolved from the same basic pattern as No. 6 by this procedure. When the axes are parallel to *a* the type is *a*21.

One other new derivative comes from 112 by starting with a basic cell of dimensions $\frac{1}{2}a \times \frac{1}{2}b$. We can then introduce reversion-translations in both directions; in consequence, alternate symmetry axes become reversion axes (and simultaneously screw axes) whilst the others also become screw-reversion axes. The new pattern has a translation equal to half the diagonal of the cell, which is therefore centred (Diagram 8). The type-symbol is accordingly *ca*12. Pattern No. 8 is of this type; when turned through a right-angle it would be called *ca*21.

Derived from 12_1 *or* 112_1. The diagram of the unit cell of a pattern of the type 12_1 contains two arrows which may be made alternately positive and negative by changing every screw axis into a screw-reversion axis. This leads to the type $12_1'1$ as illustrated in Diagram 9. When the axes are parallel to *b*, as they are in Pattern No. 9, the type is called $112_1'$.

The only other derivative of 12_1 comes by introducing a reversion-translation parallel to *b* using a basic cell whose sides are *a* and $\frac{1}{2}b$. This changes alternate screw axes into screw-reversion axes (Diagram 10). The type is $b2_11$ and Pattern No. 10 is an example. The other orientation is $a12_1$.

Derived from Type 222. Five new types can be obtained as derivatives of the type 222. It will be recalled that the basic pattern has symmetry axes in both directions, and the first counterchange type is obtained by changing all the axes in one direction (say parallel to *a*) into reversion axes. The centres of symmetry then change into reversion centres (Diagram 11), so that the type-symbol is 2′2′2. The type is illustrated by Pattern No. 11.

A second derivative has the same central symmetry as the basic pattern, but its axial symmetry is reversional in every case, so that its symbol is 22′2′ (Diagram 12 and Pattern No. 12). The other new types involve the doubling of one or both sides of the basic cell, and the introduction of reversion-translations. $b22_1$ (Diagram 13) comes from a basic cell of

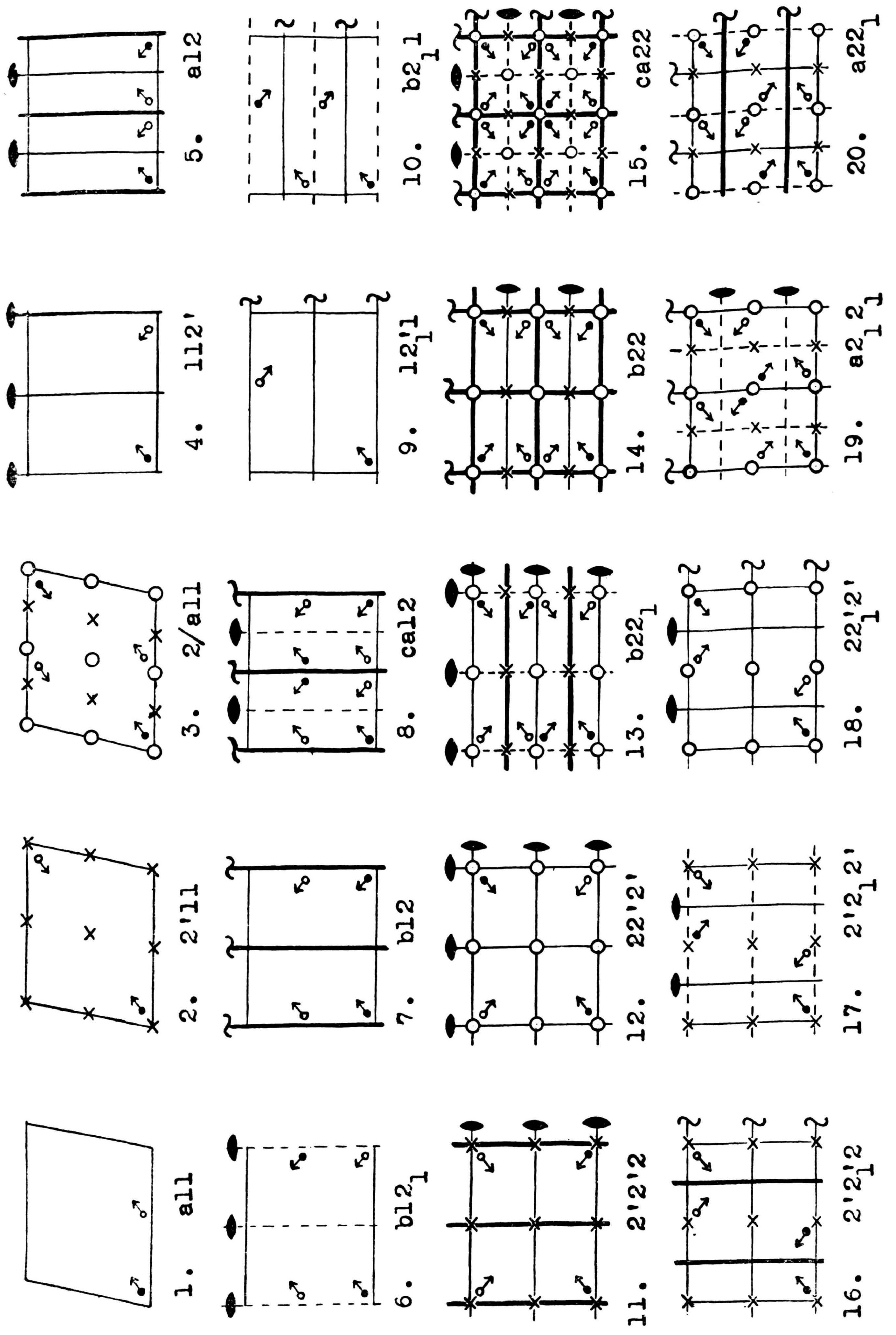


FIG. 1.

Diagrams of the cells of the first 20 types of counterchange symmetry in plane patterns. Centres of symmetry and reversion are marked by circles and crosses respectively. Heavy lines represent symmetry axes, broken lines screw axes, and the symbols ⬮ and ʔ are placed at the ends of reversion and screw-reversion axes respectively. Two types of arrows are used to denote the operation of reversal, one being regarded as the "negative" of the other.

dimensions $a \times \frac{1}{2}b$ and is obtained by changing every b-axis and every other a axis into a reversion axis; this also changes the centres lying on the remaining symmetry axes into centres of reversion, and each b-axis becomes a screw axis as well as a reversion axis. The alternative orientation of this type is $a2_12$, illustrated in Pattern No. 13.

The introduction of a reversion-translation parallel to b may also be done without disturbing the axial symmetry in this direction. This gives the type $b22$, as shown in Diagram 14. The b-axes are at the same time symmetry and screw-reversion axes, whilst the a-axes passing through centres of reversion have become reversion axes. The alternative direction for the reversion-translation occurs in $a22$, of which Pattern No. 14 is an example.

The final derivative of 222 is based on a cell whose sides are $\frac{1}{2}a$ and $\frac{1}{2}b$, and arises through the introduction of reversion-translations in both directions. The axial symmetry is changed so that alternate axes in each direction are reversion axes, and the central symmetry is such that perpendicular reversion axes intersect at centres of symmetry, as also do perpendicular symmetry axes. All other centres are changed to centres of reversion. Each symmetry axis is at the same time a screw-reversion axis and each reversion axis a screw axis. Diagram 15 shows that there is now a translation equal to half the diagonal of the cell, which is thus centred. The type-symbol is clearly $ca22$ (or $cb22$). A simple example of this type is shown in Pattern No. 15.

Derived from Type 22_12 *or* 222_1. In the type 22_12 there are symmetry axes parallel to b and screw axes (passing through centres of symmetry) parallel to a. We obtain the type $2'2_1'2$ by changing the latter into screw-reversion axes, a process which also changes the centres into centres of reversion. If, instead of the screw axes, the symmetry axes are changed, we get the type $2'2_12'$, in which, also, every centre is a centre of reversion. Diagrams 16 and 17 and Patterns Nos. 16 and 17 show the characteristics of these two types; the other orientations are $2'22_1'$ and $2'2'2_1$ respectively. A third derivative is found by changing all the axes into reversion elements, leaving the central symmetry as it was. Diagram 18 gives the unit cell of this type, $22_1'2'$. When the reversion axes are parallel to a as in Pattern No. 18, the type-symbol is $22'2_1'$.

Two other new types come from a basic pattern of the type 222_1 whose cell has sides $\frac{1}{2}a$ and b, by the introduction of a reversion-translation parallel to a. The two are distinguished by the fact that in one, $a2_12_1$, the symmetry axes have been changed to reversion axes, whilst in the other, $a22_1$, they remain as symmetry axes. In the former these reversion axes are at the same time screw axes, whilst in the other the symmetry axes are screw-reversion axes also. In each case alternate screw axes in the b-direction have become screw-reversion axes, which in $a2_12_1$ pass through chains of symmetry centres and in $a22_1$ through chains of reversion centres. The remaining centres are of the opposite kind in each case. Pattern No. 19 is an example of $a2_12_1$, and No. 20 illustrates $b2_12$, the other orientation of $a22_1$.

Derived from Type 22_12_1. The basic pattern here has screw axes parallel to a and to b, and the only derivatives are obtained by changing the axes in one or both directions into screw-reversion axes. The former procedure implies that the centres must become centres of reversion, and gives the type $2'2_12_1'$ (Diagram 21) with $2'2_1'2_1$ (Pattern No. 21) as the alternative orienta-

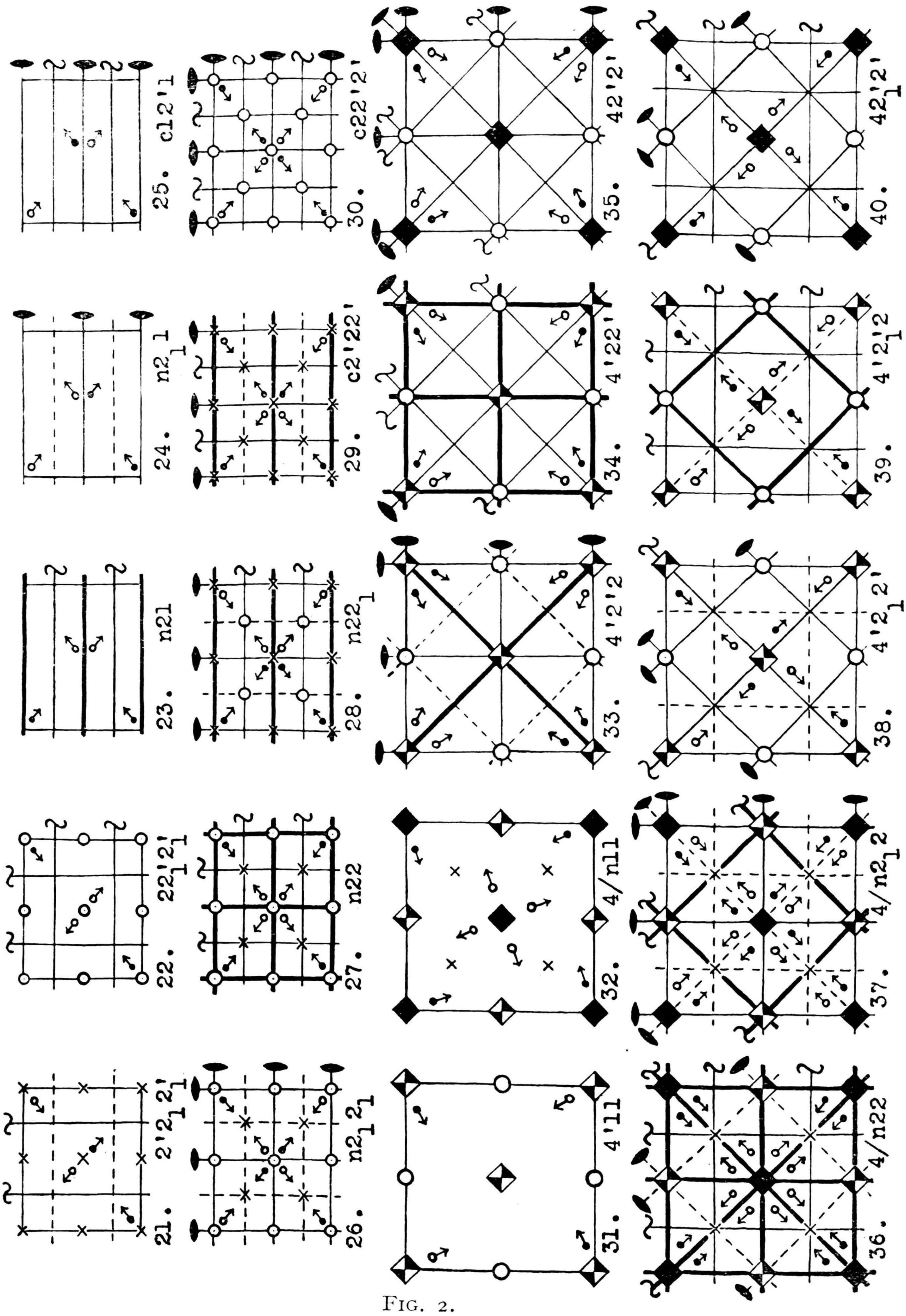
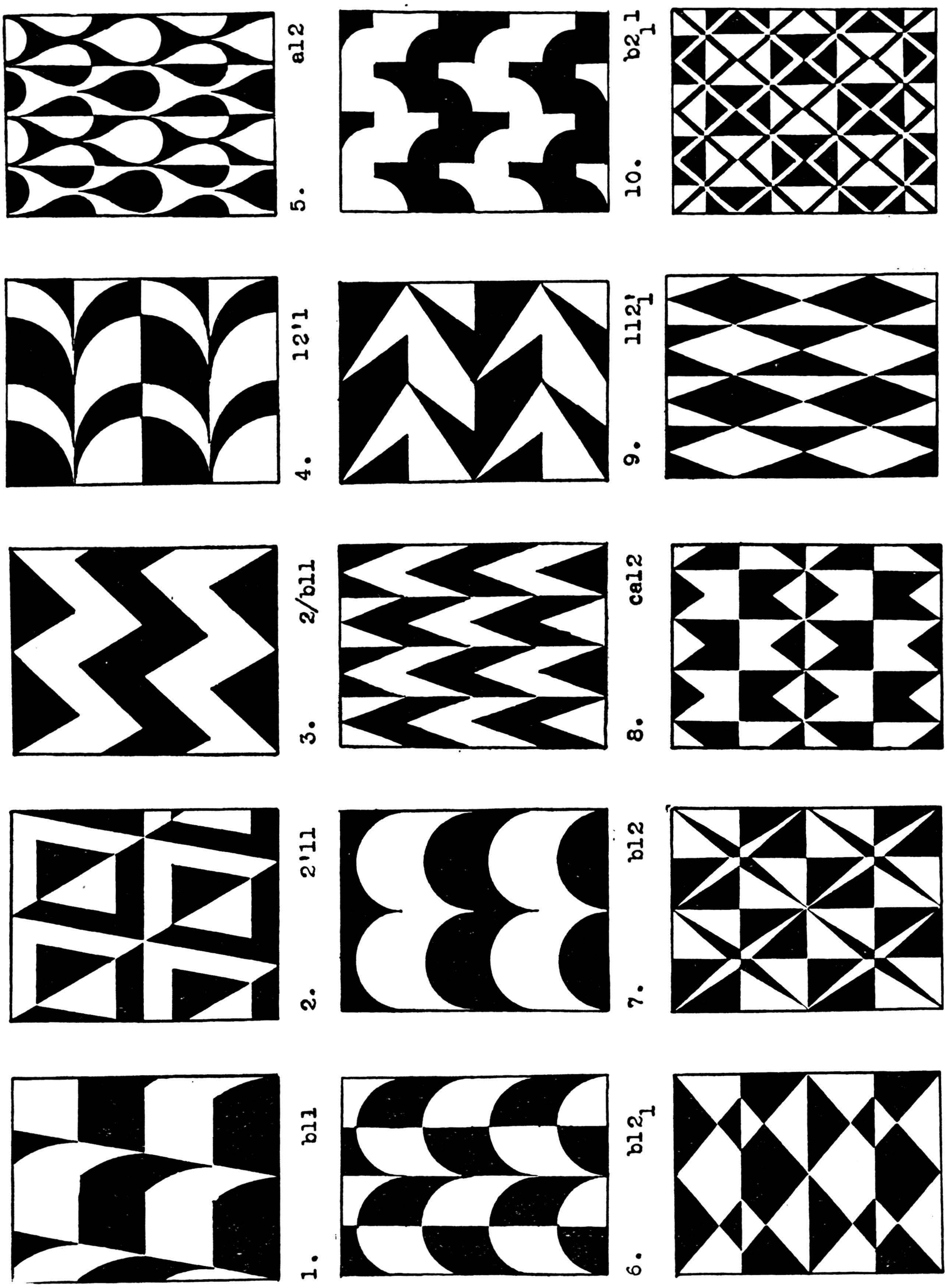


FIG. 2.

Diagrams 21-40 of the counterchange symmetry types in plane patterns. Black squares represent centres of symmetry of the fourth order, and black-and-white ones 4-fold reversion centres.

tion. In the other case the central symmetry remains unchanged and the type is $22_1'2_1'$. Diagram 22 gives the unit cell of this, and Pattern No. 22 is an example.

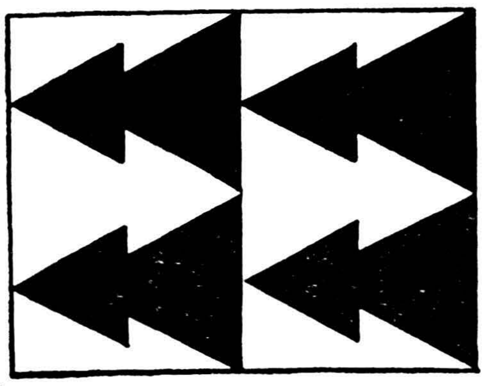
Derived from Type c12 or c112. In this type symmetry and screw axes alternate in one direction and we may change the members of one set, or of the other, or of both sets, into reversion elements. Keeping the symmetry axes and changing the screw axes gives the type *n*21, where the *n* stands for a reversion-translation parallel to the diagonal of the cell, which is no longer centred. Diagram 23 and Pattern No. 23 illustrate this type, the latter in the orientation *n*12.

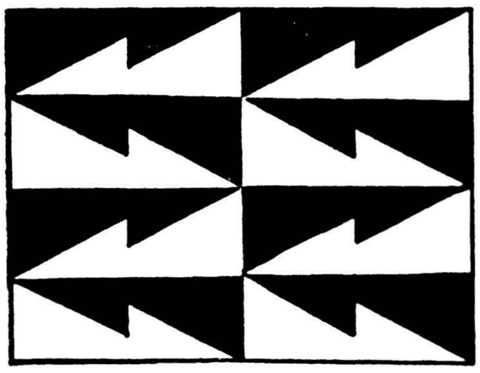


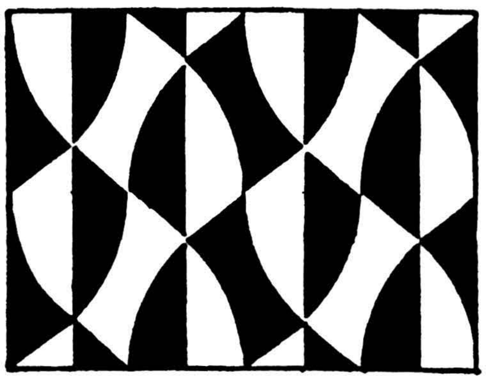
Patterns 1-15

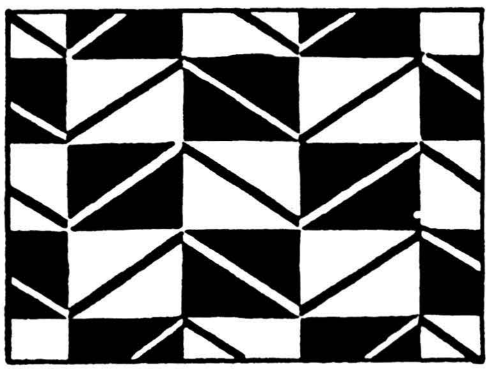
If the screw axes remain unaltered, whilst the symmetry axes change, the type $n2_1$1 is obtained (Diagram 24). When the axes are parallel to *b*, as they are in Pattern No. 24, the type is $n12_1$. The third derivative of *c*12 has only reversion and screw-reversion axes (Diagram 25) and the cell remains centred. The type is *c*12'1 when the axes are parallel to *a*, or *c*112' when they are parallel to *b*, as in Pattern No. 25.

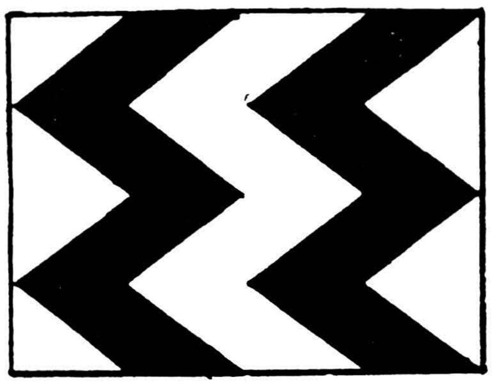
Derived from Type c222. The basic pattern has symmetry axes alternating with screw axes in both directions. If all the symmetry axes become reversion axes, whilst the screw axes are unchanged, the type $n2_12_1$ is obtained. In this, a centre of symmetry lies at the intersection of each pair of reversion axes, and a centre of reversion at the intersection of each pair of screw axes, as shown in Diagram 26. Pattern No. 26 is an example of $n2_12_1$. A second possibility is that the screw axes should become screw-reversion axes, whilst the symmetry axes remain unchanged; the centres lying on screw-reversion axes then become reversion centres (Diagram 27). The type-symbol is $n22$, and a very simple pattern of this type is given in No. 27.

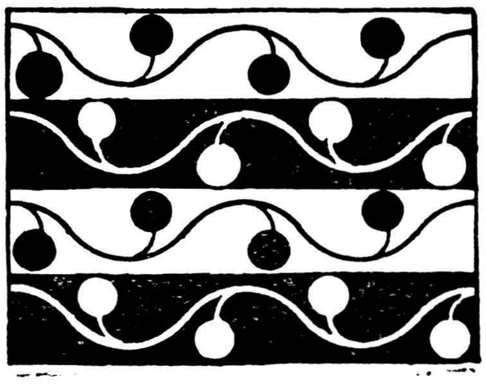

16. $2'2'2_1$

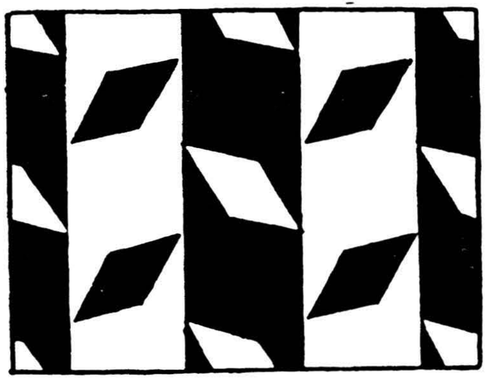

17. $2'2_12'$

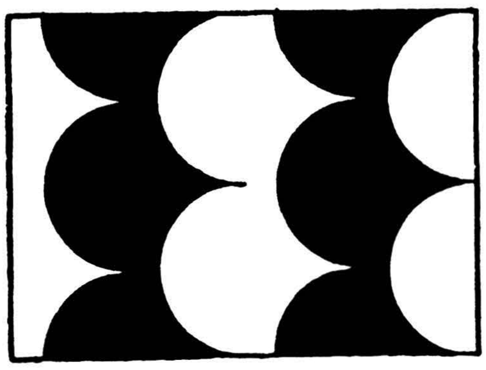

18. $22'2'_1$

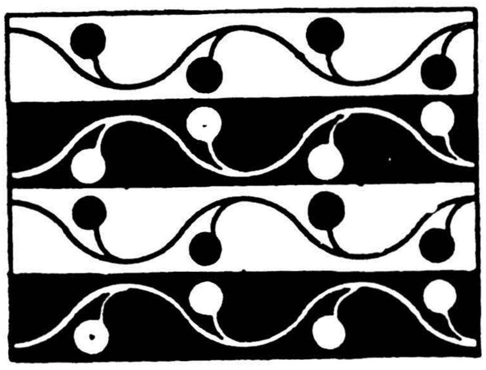

19. $a2_12_1$

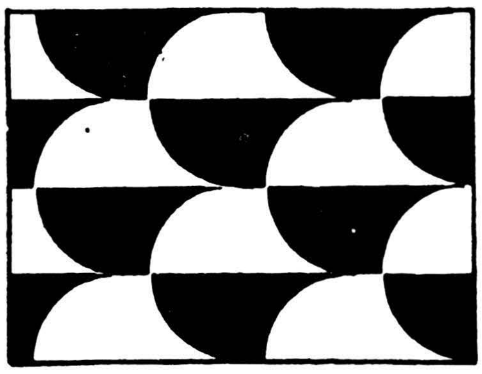

20. $b2_12$

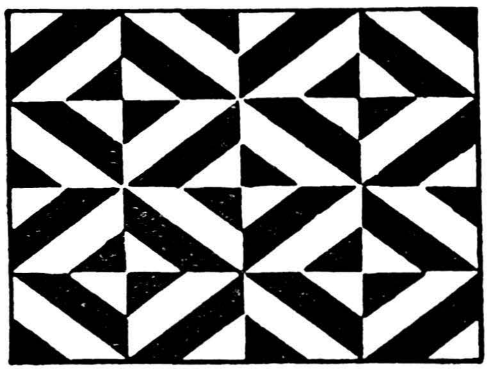

21. $2'2'_12_1$

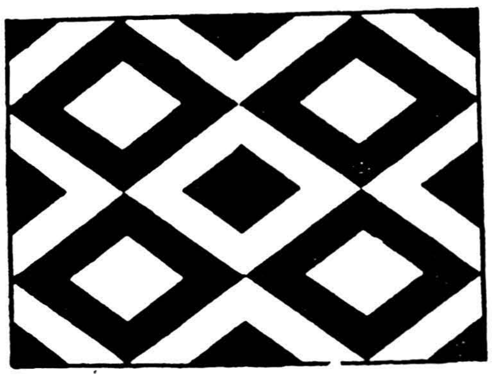

22. $22'_12'_1$

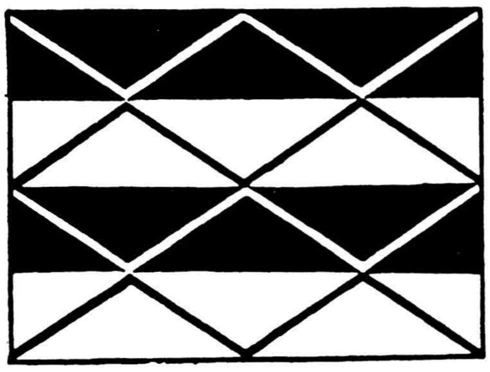

23. $n12$

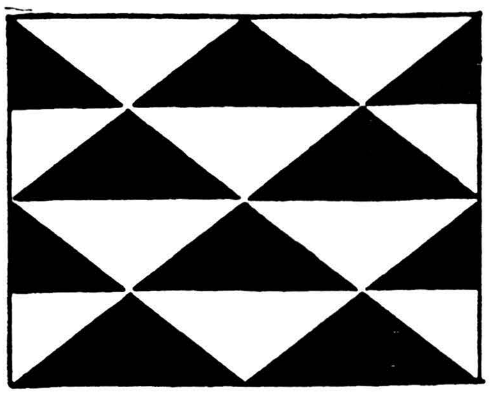

24. $n12_1$

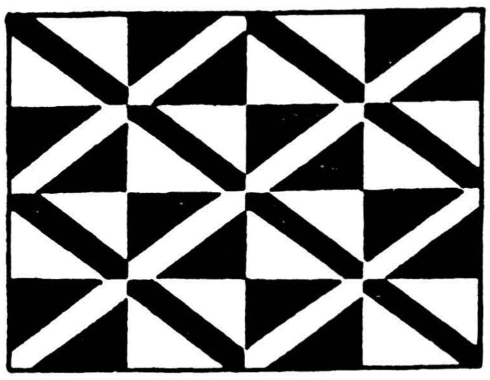

25. $c112'$


26. $n2_12_1$


27. $n22$


28. $n22_1$


29. $c2'22'$


30. $c22'2'$

Patterns 16-30

Two other types are found by treating the axes in the two directions differently. In $n22_1$ the symmetry axes parallel to *b* and the screw axes parallel to *a* have been changed to reversion elements (Diagram 28 and Pattern No. 28). In the other of these two derivatives, *c*2'22', all the axes in the *a* direction are unchanged, but all those in the other direction and also all the centres become reversion elements. Diagram 29 shows that the cell still remains centred, and Pattern No. 29 is one of this type.

The last derivative of *c*222 is obtained by changing every axis into a reversion element, leaving all the centres unaltered. Here, too, the cell remains centred, so that the type is *c*22'2' (Diagram 30 and Pattern No. 30).

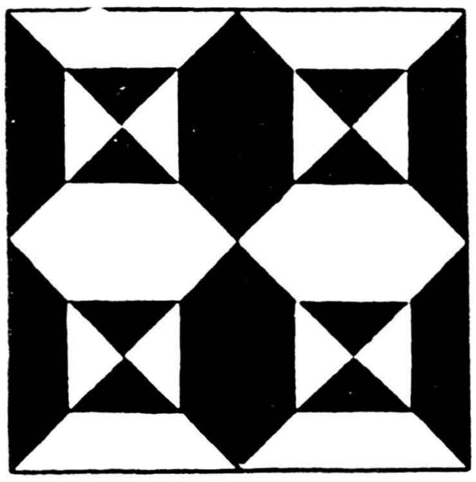
Derived from Type 4. The first and simplest derivative of this type is 4'11, which comes by changing every 4-fold centre into a 4-fold centre of reversion, leaving the centres of the second order as they were. Diagram 31 and Pattern No. 31 illustrate the type. Starting with a pattern of the type *c*4 (that is, one constructed in a centred square net), Pattern No. 32 was obtained by leaving the net points as centres of 4-fold symmetry and changing the other 4-fold centres into centres of reversion. The unit cell is shown in Diagram 32, and it will be seen that the central symmetry of the second order is also reversional. The type symbol is 4/*n*11, the *n* denoting a reversion-translation along the diagonal of the unit cell.

Derived from Type 422. This type has both primary and secondary symmetry axes (see Part III). If the former are changed to reversion axes, a change necessitating the alteration of the 4-fold centres into reversion centres if the secondary symmetry axes are retained, a new type, 4'2'2 is obtained. The unit cell is shown in Diagram 33, and it will be seen that the secondary screw axes and the centres of the second order also remain unchanged. An example of this type is given in Pattern No. 33.

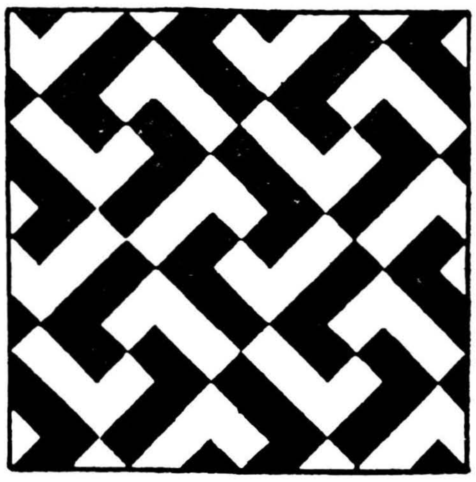
A type in many respects similar to the last is obtained by retaining the primary symmetry axes of 422, but converting all the secondary axes (both symmetry and screw) into reversion elements. This type, 4'22', has the same central symmetry as 4'2'2 (Diagram 34). The example shown (Pattern No. 34) is based on Pattern No. 11 (Part III). A rather curious relation exists between 4'2'2 and 4'22', which may be seen as follows. If the unit cell of the diagrammatic form of 4'2'2 (it contains four positive and four negative arrows) is *centred* by the introduction of eight more arrows round the centre of the cell, arranged so that in going round in a counter-clockwise direction from the horizontal there are alternately two positive and two negative arrows, the symmetry of the resultant pattern is the same as that of 4'22'. For symmetry axes now appear in the original positions of screw axes, and new screw-reversion axes become evident midway between pairs of adjacent parallel reversion axes, and this is just the disposition of axes in Diagram 34 when it is turned through 45° (the central symmetry is also changed to correspond with the smaller unit cell). In the same way, by centring the unit cell of 4'22' we obtain a pattern of the type 4'2'2 with a smaller unit cell oriented at 45° with respect to the original one.

The third derivative of 422 is found when every axis is changed to a reversion element, leaving the central symmetry unaltered. This type is 42'2', and it shares with $4/n2_12$ (see below) the distinction of having reversion axes both in the primary and secondary positions. In consequence it is impossible to construct a pattern of either type on " point paper " on account of the necessary appearance of an angle of 45° at the intersection of two reversion axes (see Pattern No. 35).

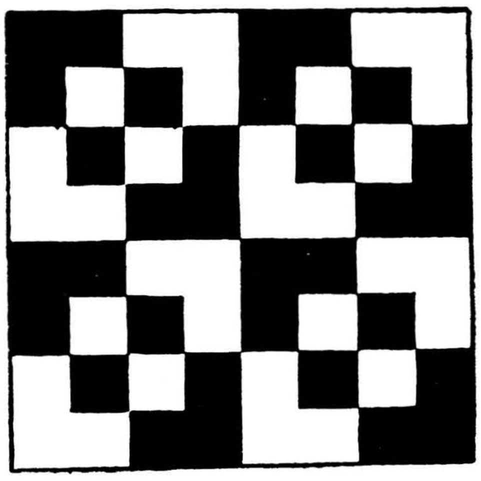
The remaining two types which can be derived from 422 require a basic pattern constructed in a centred-square net. In each the net points are still centres of 4-fold symmetry, but all the other centres are changed to centres of reversion. 4/*n*22 (Diagram 36) has four symmetry axes through the centre and each corner of the cell, and of these the secondary ones are also screw-reversion axes, whilst interleaving these are sets of screw axes which are simultaneously reversion axes. A screw-reversion axis lies midway between each pair of adjacent primary symmetry axes. Pattern No. 36 illustrates 4/*n*22 ; it may also be noted that the ordinary chess-board or "plain weave" pattern is of this type, but as usually drawn would be in the orientation *c*4/*a*22.



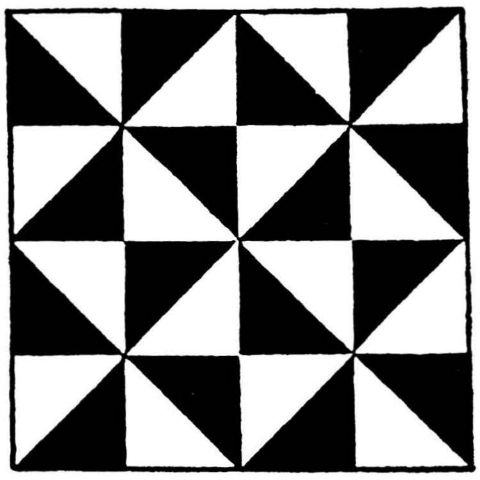
34. $4'22'$



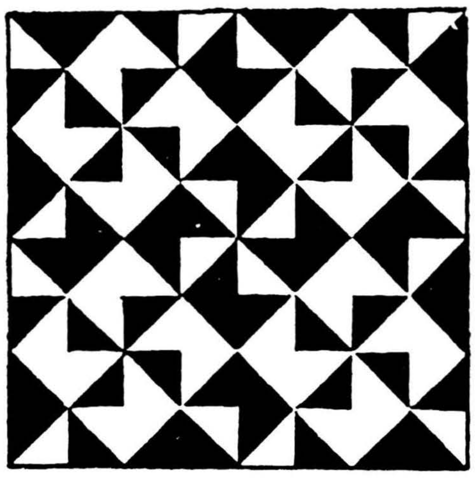
33. $4'2_12'$



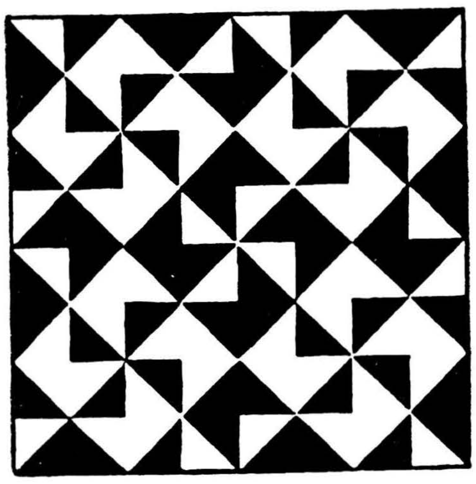
33. $4'2'2$



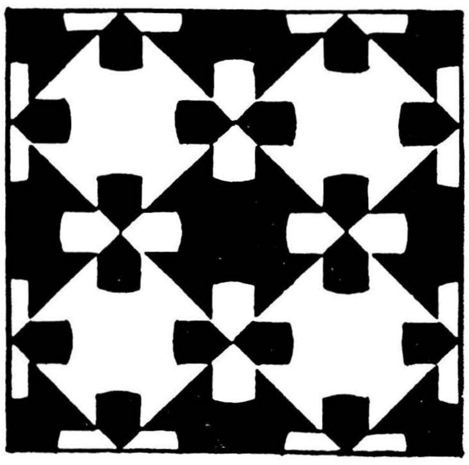
37. $4/n2_12$



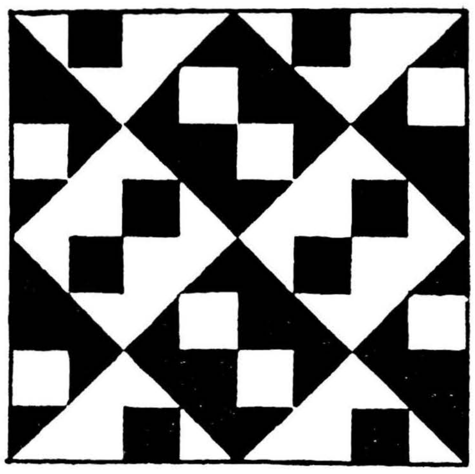
40. $4\,2'_12'$



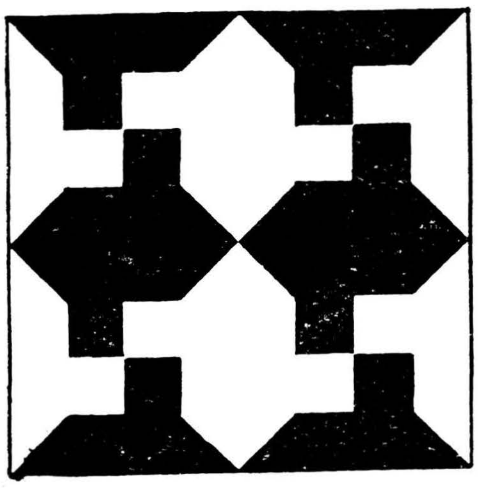
32. $4/n11$



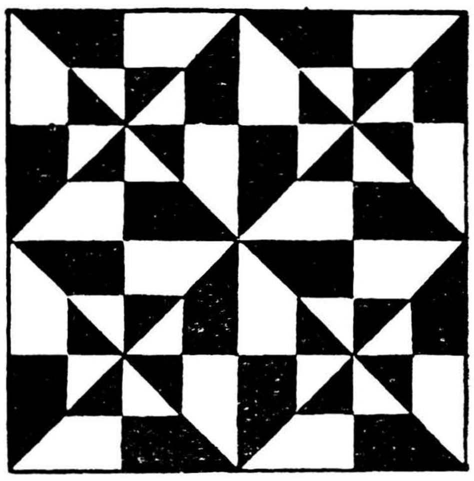
36. $4/n22$



39. $4'2'_12$



31. $4'11$

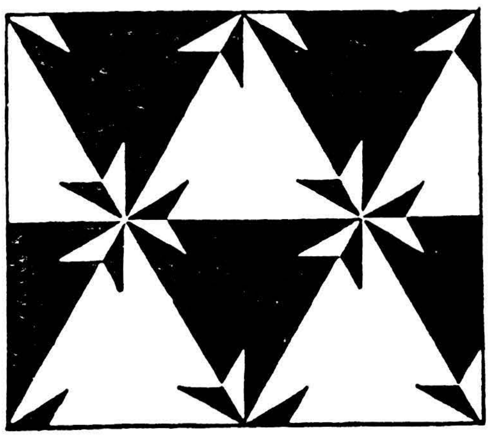


35. $42'2'$

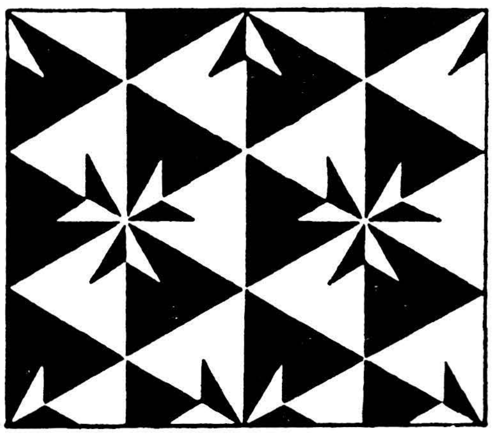
Patterns 31-40

The remaining derivative is $4/n2_12$, which was referred to above. Its central symmetry is the same as that of $4/n22$, but it has reversion and screw-reversion axes where the other has symmetry and screw axes, and *vice-versa*. The cell is shown in Diagram 37, and Pattern No. 37 shows the way in which angles of 45° make their appearance in any example.

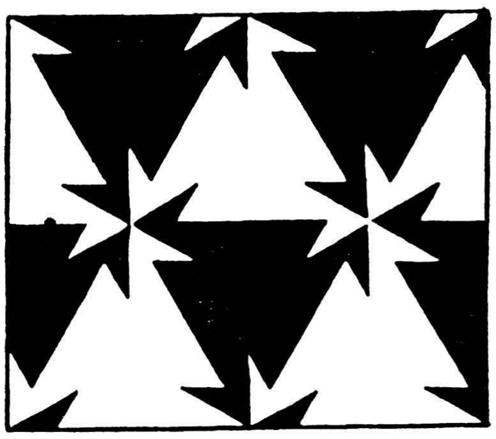
Derived from Type 42_12. The basic pattern has primary and secondary screw axes and secondary symmetry axes. Changing the latter to reversion axes and at the same time introducing 4-fold centres of reversion instead of the 4-fold symmetry centres gives the type $4'2_12'$, whose unit cell is shown in Diagram 38. The secondary axes have all been changed, since the screw axes in this position have become screw-reversion axes. Pattern No. 38 illustrates the type ; examples have a habit of appearing rather complicated on account of the lack of symmetry axes.



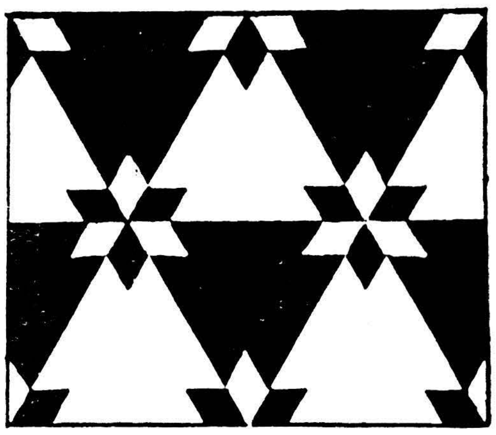
41. **32'1**



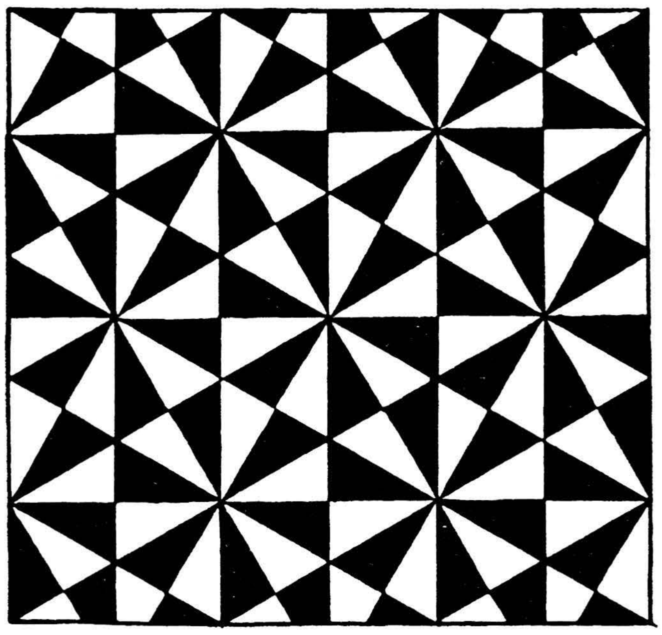
42. **312'**



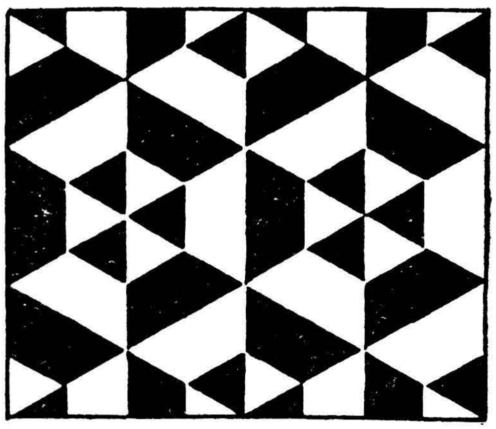
43. **6'**



44. **6'2'2**



46. **62'2'**



45. **6'22'**

Patterns 41-46

If, instead of the secondary axes, the primary ones are changed to reversion elements, whilst of the centres of symmetry those of the fourth order are also changed, we obtain the type $4'2_1'2$, shown diagrammatically and in practice in Diagram 39 and Pattern No. 39. The final derivative of 42_12 has the normal central symmetry, but every axis has become a reversion element. This type is $42_1'2'$ (Diagram 40). The difference between Patterns Nos. 40 ($42_1'2'$) and 32 ($4/n11$) is at first sight almost imperceptible. It depends on the sense of " rotation " of the central swastika-like figure, and the difference here is responsible for the appearance of the axes in $42_1'2'$.

The remaining counterchange types are of less interest to the textile designer, as they are based on hexagonal nets. Brief descriptions of them follow.

Derived from Type 321. There is but one counterchange type which is based on 321, and this is obtained by changing every axis into a reversion element, leaving the central symmetry unaltered. Diagram 41 shows the centred cell of this type, 32′1, and the example, Pattern No. 41, comes directly from No. 14 (Part III) by the method described.

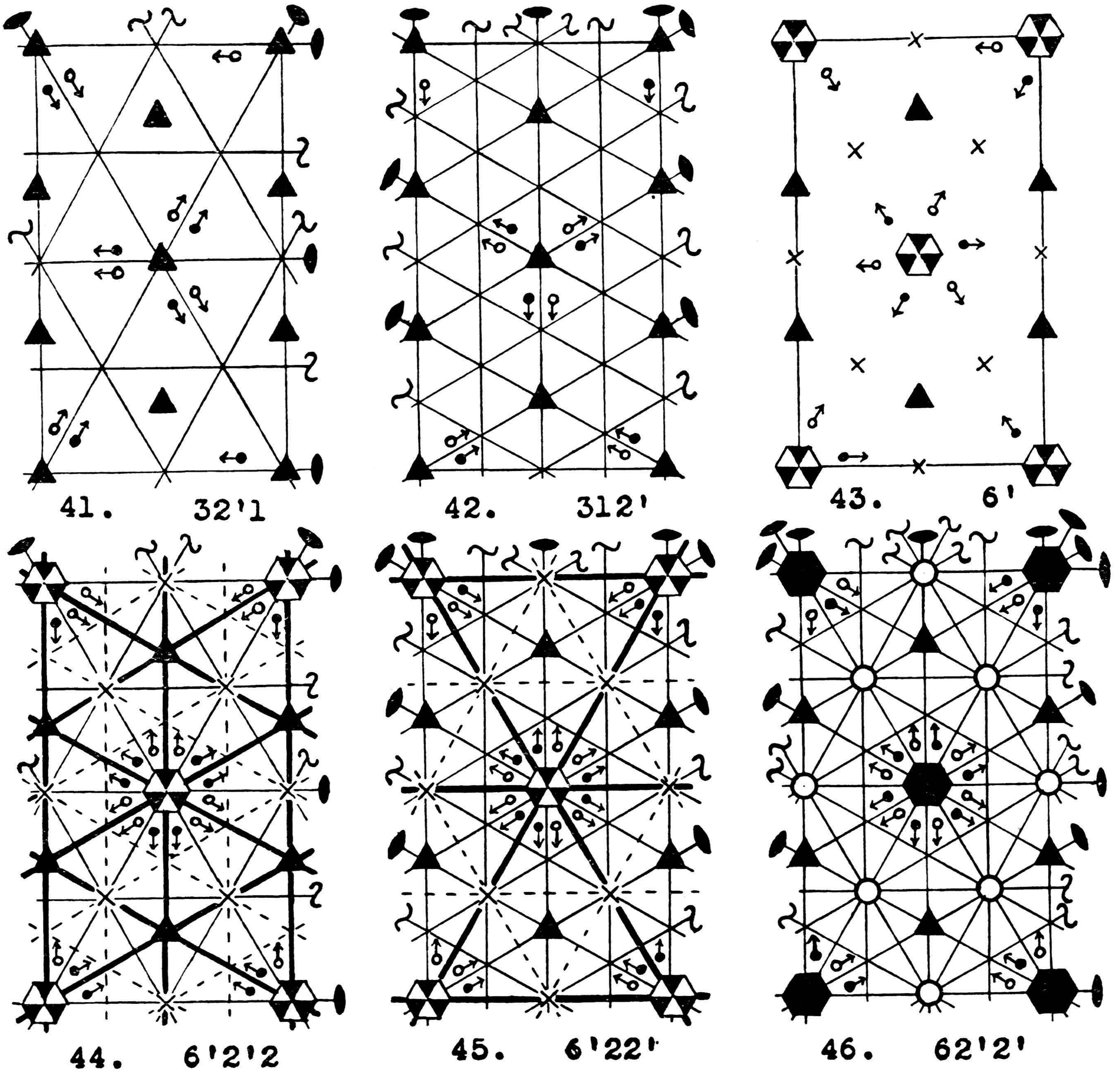

41. 32'1
42. 312'
43. 6'
44. 6'2'2
45. 6'22'
46. 62'2'

FIG. 3.

Diagrams 41-46 of the counterchange symmetry types in plane patterns. Black triangles and hexagons represent symmetry centres of the 3rd and 6th orders, respectively, and black-and-white hexagons 6-fold reversion centres.

Derived from Type 312. Here, too, the only derivative is obtained by changing all the axes into reversion elements, as shown in Diagram 42. Pattern No. 42, which is based on No. 15 (Part III), is the example of this type.

Derived from Type 6. The only possible procedure in this case for the derivation of a new type is the alteration of all the even-order centres of symmetry into reversion centres, leaving the 3-fold centres unchanged. This gives a cell of the sort shown in Diagram 43. Pattern No. 43 was obtained from a basic one consisting of six small scalene triangles arranged round each net point by the method described.

Derived from Type 622. In this case there are two classes of derivatives distinguished from each other by the highest point symmetry, which may be either 6′2 or 62′. In the former case there are two types, whose characteristics depend on whether the symmetry axes are primary or secondary. When they are secondary, we get the type 6′2′2 (Diagram 44), whose central symmetry is like that of 6′, and whose primary axes are all reversional. Pattern No. 44 is of this type. The other member of this class, with primary symmetry axes, is 6′22′, shown in Diagram 45 and Pattern No. 45. A general resemblance exists between the types 6′2′2 and 32′1, in the sense that both tend to have a background of large black-and-white triangles; and so 6′22′ and 312′ tend to be divided into smaller triangles. These triangles are bounded by the reversion axes shown in the various diagrams.

The final derivative of 622, with the point symmetry 62′, is 62′2′; it has the same central symmetry as 622, but every axis is a reversion element. Diagram 46 shows the centred cell of such a pattern, and the example given (Pattern No. 46) illustrates how highly symmetrical this type is. This pattern is perhaps the most simple one of the type 62′2′.

APPENDIX

(i) *The limitations imposed on the net of a pattern by its counterchange symmetry elements.* In Part III it was shown that in certain cases the occurrence of symmetry elements other than translations imposes restrictions on the net of the pattern. Notably, symmetry or screw axes can only occur in directions in which the net is axially symmetrical; centres of the fourth order are only present when the net is square and centres of the third or sixth orders when the net is hexagonal. These results are easily extended to cover the counterchange patterns:—whenever there is a symmetry, reversion, screw, or screw-reversion axis the net must be axially symmetrical about axes in the same direction; and the limitations imposed by centres of reversion of the fourth and sixth orders are the same as those due to the corresponding centres of symmetry. Only centres of the second order, geometrical or reversional, have, on their own account, no restrictive influence on the type of net, so that patterns in ordinary nets can have these kinds of symmetry elements but cannot have any axes or centres of higher orders.

(ii) *Reversion-translations.* If t is any translation of a pattern, a possible counterchange operation is a translation equal to $\frac{1}{2}t$ followed by a reversal. We shall show that when a pattern has such a reversion-translation as a symmetry operation then, whatever t may be and whatever unit cell is chosen, there must be a reversion-translation along one of the sides or along a diagonal of the unit cell.

Let OACB (Fig. 4) be the unit cell, and suppose that OQ represents the translation t. With reference to co-ordinate axes along OA$=a$ and OB$=b$, the co-ordinates of Q are then $(\lambda a, \mu b)$, where λ and μ are integers. Since OP represents a reversion-translation, P, whose co-ordinates are $\left(\frac{\lambda a}{2}, \frac{\mu b}{2}\right)$, is not a net-point, and hence λ and μ are not both even.

Let R be any other net-point, so that OR is a translation of the pattern. Then RP must represent the translational part of a reversion-translation, since $\overline{\text{OR}} + \overline{\text{RP}} = \overline{\text{OP}}$. In particular, R may be one of the corners of the unit cell within which or on one of whose sides P lies. Three possibilities have to be considered: either λ is odd and μ even, or λ is even and μ odd, or

λ and μ are both odd. For Q in Fig. 4 the first alternative holds. R is then taken as the net-point $\left(\frac{\lambda-1}{2}a, \frac{\mu}{2}b\right)$, and RP is equal and parallel to $\frac{1}{2}$OA. In the second case, R is taken as $\left(\frac{\lambda}{2}a, \frac{\mu-1}{2}b\right)$, and RP is equal and parallel to $\frac{1}{2}$OB. The third possibility is illustrated by the point Q′ in the figure ; R′ is then $\left(\frac{\lambda+1}{2}a, \frac{\mu+1}{2}b\right)$, and R′P′ is parallel to, and half of, the diagonal OC of the unit cell. It should be noted that the three alternatives are mutually exclusive, so that no pattern can have, for instance, reversion-translations along both sides of the *unit* cell. Also, in the last mentioned case we can, if we wish, take a new unit cell having one side along OC, so that in any pattern with a reversion-translation it is possible to take a unit cell such that there is a reversion-translation along one of its sides. We may suppose that this is done in those cases where the change of shape of the unit cell is of no importance, that is, in patterns in ordinary nets. The use of the symbol n may in this way be restricted to patterns in rectangular or square nets.

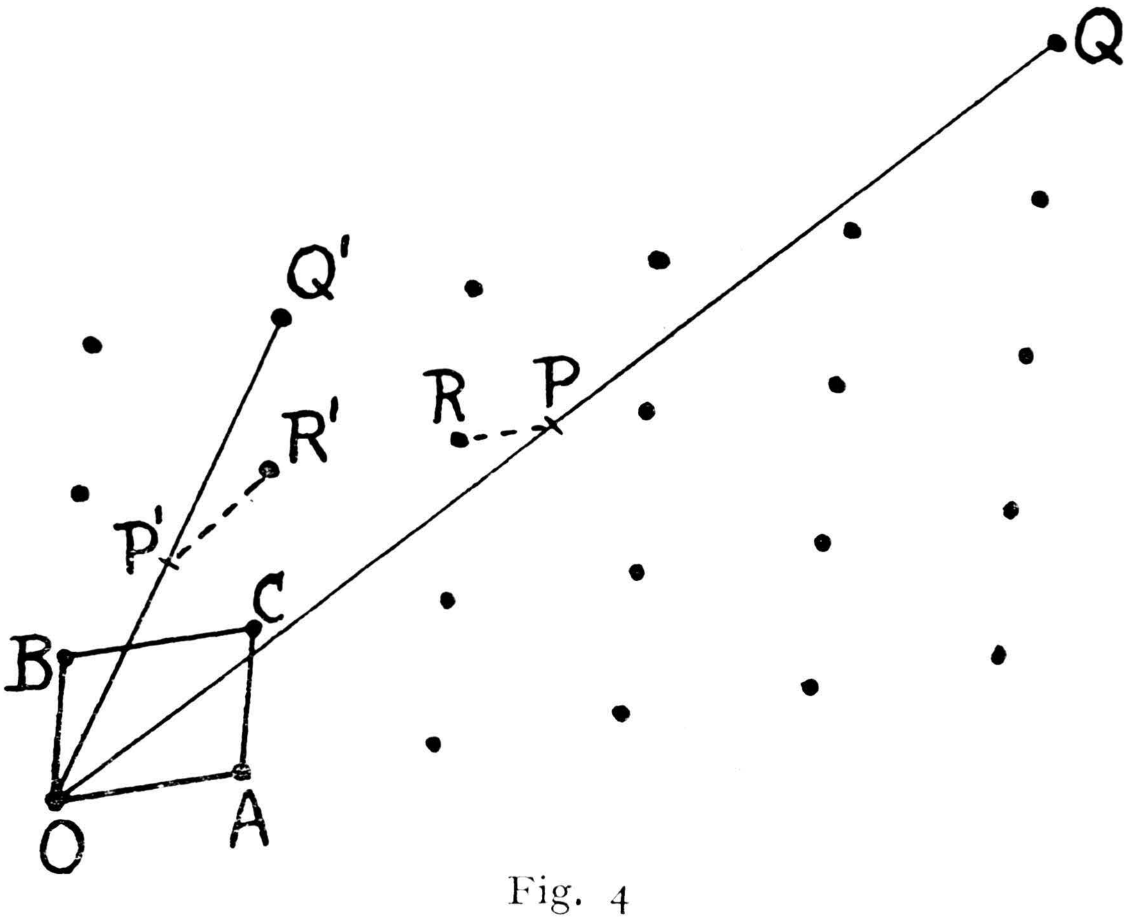


Fig. 4

(iii) *The " basic pattern."* The diagrams given in Part III as representing the 17 fundamental types, when extended to cover an indefinite number of cells, are such that any movement taking an arrow to the initial position of another interchanges all the arrows amongst themselves, i.e., is a symmetry operation. In the corresponding diagrams for the counterchange types the symmetry operations interchange the positive arrows amongst themselves and also the negative ones. Any movement taking an arrow to the original position of one of the other kind interchanges all the positive with all the negative arrows, i.e., it is the geometrical part of a counterchange operation. If in such a figure we suppress the operation of reversal, so that the distinction between the two kinds of arrows is lost, we arrive at a new diagram which is such that a movement taking an arrow to the initial position of any other interchanges all the arrows amongst themselves, i.e., we obtain one of the 17 fundamental diagrams. This is the basic pattern for the counterchange type under consideration.

In the text we proceed in the reverse direction, deriving the counterchange types from the fundamental ones. To do this it is necessary to know the relationship which exists between the unit cells of the basic pattern and its derivative. It is clear that suppression of reversal can only alter the translational symmetry if the counterchange pattern has reversion-translations, so that if it has none the unit cell of the basic pattern is the same as that of the derived one. When reversion-translations occur these become translations in the basic pattern, and this means that there is a change in the unit cell, a change which, according to the result obtained in (ii) above, may be either a decrease to half the length in the direction of one of the sides or else a change of shape to take into account the new translation along the diagonal.

In the case of ordinary nets we have shown how, by a suitable choice of cell, consideration may be restricted to the first of these alternatives. For the unit cell of a pattern derived from types 1 and 2 we need therefore consider only the basic cell itself or one twice as long in the direction of one of its sides. If the derived cell is rectangular, however, the basic cell must be either (*a*) the same as the derived cell, or (*b*) rectangular and half as long in the direction of *a* or *b*, or (*c*) centred-rectangular but of the same dimensions as the derived cell.

In the case of a derived cell which is rhombic (suitable for, and therefore considered in the pattern-types only in connection with, patterns having axial symmetry of some sort) the basic net must be axially symmetrical. This rules out the first alternative, since a net based on a unit cell obtained by dividing a rhombus into two equal parts by a line parallel to one of its sides is not axially symmetrical. The basic net for a rhombic counterchange pattern must therefore be either (*a*) the same as the derived one, or (*b*) obtained from the derived one by " centring " the unit cell. In this case the basic net is rectangular, and its unit cell is of half the lateral dimensions (and therefore quarter the area) of the *centred-rectangular* cell of the derived pattern.

A counterchange pattern requires a square unit cell if it is to have centres of symmetry or reversion of the fourth order. The basic pattern will then also require a square net, and either its unit cell or its centred double cell will be of the same size as the unit cell of the derived pattern (no pattern with centres of symmetry or reversion of the fourth order can have a reversion-translation parallel to a side of its unit cell, since this would imply another along the other side).

Finally, no pattern with centres of the third or sixth orders can have a reversion translation at all,* for its basic pattern would require a net which must be simultaneously hexagonal (on account of the central symmetry) and rectangular (as in the basic pattern for a rhombic counterchange pattern). The derived and basic patterns must therefore have the same cells.

It will be seen therefore that in no case is it necessary to extend the cell of the basic pattern (as given in Part III) to more than twice its lateral dimensions in order to obtain the requisite amount of detail for the cell of the counterchange pattern. For the rest, the procedure is quite straightforward, as in the text.

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* The fundamental type 3 is therefore unique in having no counterchange derivatives, for the only symmetry operations for such a pattern are translations and rotations about centres of the third order. The latter cannot have reversals added to them, and reversion-translations are impossible in hexagonal patterns.

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