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Report No. 1

Synthetic Resin Glues:

Preliminary Study of Factors Affecting the Strength of Glued Joints in Aluminium Alloys

(Based on Ministry of Aircraft Production Scientific and Technical Memorandum No. 16/46, March, 1946) by W. J. Roff and K. W. Pepper, Department of Scientific and Industrial Research

U.D.C. No. 668.3 : 669.715

Abstract

A glue based on a mixture of polyvinyl acetate and phenol-formaldehyde resin in methanol solution was examined in simple lap-joints. It was found that the composition of the mixture of the glue, i.e. the proportion of the polyvinyl acetate to phenol-formaldehyde, had a major effect on the strength of the joints. The development of a glue, method of testing, appearance of joints after testing, study of variations in composition of syrups on joint-strength and on other properties of the glue, and the effect of variations in the conditions of bonding are described. Appendices give standard procedure adopted in making test joints with R./4. glue, reproducibility in strength of joints, strength of Alclad joints, and results for R.A.E.-type joints and results for a commercial glue.

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Illustrations

I. Introduction

During recent years a number of adhesives have been introduced for making joints in aluminium alloys. Despite certain defects, e.g. poor resistance to tearing stresses, the strength of glued joints is sufficiently high to merit consideration of the use of adhesives in stressed aircraft structures. It has been claimed that the shear strength of glued lap-joints exceeds the strength of comparable rivetted or spot-welded joints.* The chief advantage to be gained from glued joints would not, however, be increase in strength, but greater facility in the production of structures possessing a very smooth surface. Other advantages claimed are that glued joints are pressure-tight and since the adhesive layer is a non-conductor the possibility of electrolytic corrosion in joints between dissimilar metals is reduced. Apart from application in aircraft construction, a reliable adhesive could be widely used with light alloys in many industries.

The main criticism of existing glues is that the technique of joint-fabrication is critical and not suited to full scale production. As inspection of all glued joints is virtually impossible it is essential that the reproducibility of joints glued by production methods should be of a high order. But with existing glues and techniques, much care is required even in the laboratory to make reliable joints.

This report describes preliminary work attempting to overcome these disadvantages. The objective has not been a glue of higher strength than those already available, but development of glues and techniques which are simpler in application and more reliable in results. To this end, it was proposed to examine systematically the effect of each factor involved in the fabrication of joints, hoping thereby to reveal those which are critical.

II. Development of a Glue Suitable for Study

Many of the existing glues consist of mixtures of a linear polymer, e.g. a polyvinyl acetal or synthetic rubber, with a cross-linking resin, e.g. phenol-formaldehyde or urea-formaldehyde. Preliminary tests proved that a simple mixture of this type would be satisfactory for further study. This mixture, which was designated R./4.50, consisted of equal parts by weight of an aqueous emulsion of polyvinyl acetate and an aqueous solution of phenol-formaldehyde resin. The mixture was thinned with methanol to a "syrup" of suitable viscosity. In later work, the aqueous emulsion of polyvinyl acetate was replaced satisfactorily by a solution of the polymer in aqueous methanol.

The syrup could be spread evenly on clean aluminium strips and dried, on evaporation of the solvents, to a tacky film. If the coated strips were pressed together by hand at the tacky stage, then held lightly by clips and baked, good joints resulted. This was the principle on which R./4. joints were developed; details of the preparation finally adopted are to be found in Appendix 1, an outline of which is given :—

1. Syrup was applied as a paint to the metal surfaces which had been previously cleaned, degreased (in trichlorethylene vapour), pickled (in sulphuric-chromic-acid mixture), washed and dried.
2. Coated strips were then left for evaporation of the solvent until nearly dry (tacky), then pressed tightly together by hand and secured with clips supplying light pressure (< 50 pounds per square inch).
3. Clipped joints were baked at 105° C. for 20 hours.

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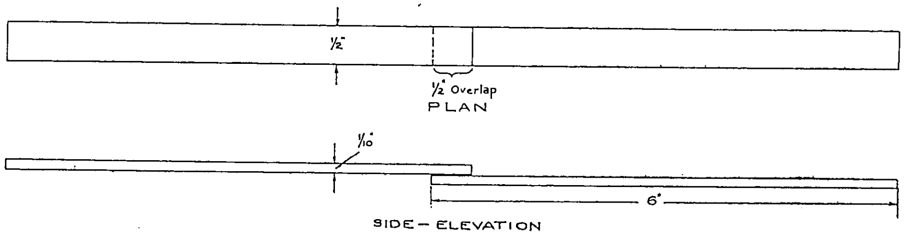
*Adhesives for Metals ; N. A. de Bruyne ; Metal Industry, September 14, 1945.

III. Methods of Testing

Laboratory evaluation of any glue presents considerable difficulty. Even with wood glues, where the results of laboratory tests can be checked against experience gained from the performance of plywood, etc., over many years, completely satisfactory tests have yet to be developed.

From a fundamental point of view, it would be desirable to use a test which measures a single property of the glued joint, e.g. static strength in pure shear. Even if it were possible to devise such a test, it is doubtful if the results would have much significance when considering actual structures glued by production techniques, because only rarely in service are glued joints subjected to a single type of stress. A compromise is thus unavoidable and in this work a simple lap-joint, $\frac{1}{2}'' \times \frac{1}{2}''$ in $\frac{1}{10}''$ duralumin (see Fig. 1) was chosen, for the following reasons :—

1. The metal strips could be cut with good control of dimensions and flatness without difficulty. Moreover, each strip could be used for four tests.
2. The lap-joints could be made simply and rapidly. This was an advantage because it was desirable to carry out a large number of tests.
3. When a lap-joint is pulled in tension the glue is sheared, but owing to bending of the test-piece, tearing forces are also involved at the ends. Hence a glue possessing poor resistance to tearing would not give high values in this test, as might occur if the test-piece measured pure shear strength (or pure tensile strength, see results for butt-joints in Section VII (f)).



Material: Duralumin 5.L.3.

Fig. 1. C.R.L. HALF-INCH LAP-JOINT FOR TESTING METAL GLUES

The preparation and cleaning of the metal strips is described in detail in Appendix 1. All tests, with the exception of those given in Appendix 2(1) were made in the Engineering Division, National Physical Laboratory, on an Avery testing machine set to a no load strain rate of 0.3″ per minute. The results are expressed as failing *loads* (in lb.), since it is known that the apparent failing *stress* of a glued joint is dependent on the dimensions of the joint.

IV. Appearance of Joints after Testing

When glues were examined by means of the lap-joint just described, five similar joints were usually made and each joint inspected after failure and its appearance noted. One type of failure was usually consistent throughout any given set, but occasionally differential effects appeared superimposed on some but not all joints of a set. Fig. 3 shows three distinct types of failure.

A. *Differential Strain.* In this type of failure which usually denoted weak joints glue remains attached to the least strained portions of the metal. The main cause of this effect can be seen diagrammatically by reference to Fig. 2.

B. *Cohesion Failure.* Failure occurred evenly throughout the glue layer, leaving smooth surfaces coated with glue. This type of failure indicated good metal adhesion and not necessarily a weak glue.

C. *Mixed Adhesion-Cohesion,* where the glue failed unevenly in patches, leaving a rough surface on each half of the joint. This type of failure was usually associated with the highest joint-strength, the inequality and coarseness of appearance varied somewhat but it was noted that, although in places failure occurred very close to a metal surface, a really clean break was never observed and a thin film or discolouration always remained on the metal at such spots.

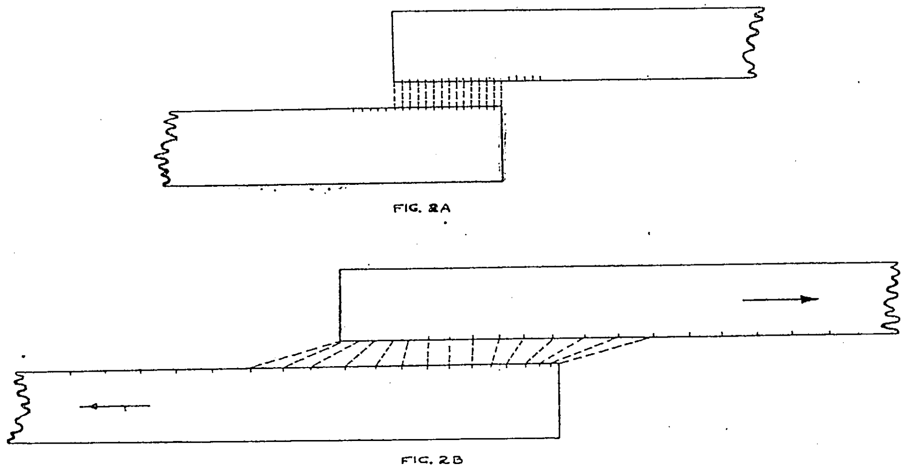


Fig. 2. A. DIAGRAMMATIC REPRESENTATION OF UNSTRAINED LAP-JOINT

B. DIAGRAMMATIC REPRESENTATION OF LAP-JOINT UNDER TENSION, SHOWING STRAIN IN METAL

(N.B.—In this diagram the extension of the metal has been exaggerated and the effect of the bending couple, to which the joint is also subjected in practice, has been omitted.)

A secondary phenomenon, frequently noted but unexplained, was the occurrence of a dendritic pattern in the glue layer. It seemed unrelated to methods of fabrication, e.g. possible inclusion of air, etc., and did not markedly affect joint-strength by its presence or absence. Fig. 3 (*d*) shows an enlargement of an extreme example of one of these tree-like patterns.

V. Study of Factors Affecting Reproducibility

The duralumin strips as received from the workshop were contaminated with traces of grease and with the oil used for cutting. In this condition they were unsuitable for use. The effect of various cleaning treatments on the strength of joints was therefore examined. (See Table 1.)

TABLE 1. EFFECT OF INITIAL TREATMENT OF METAL SURFACE ON THE STRENGTH OF JOINTS

Treatment of surface	Failing load (lb.)	Mean (lb.)
As received from workshop	100, 85, 80, 65	82
Washed in warm soapy water, rinsed and dried	100, 135, 200, 125	140
Degreased in trichlorethylene vapour	680, 605, 625, 735	661
Washed and degreased, as above	640, 570, 830, 875	729
Degreased, as above, and pickled in chromic acid to D.T.D. 915A.	765, 850, 885, 835	834

It will be seen from Table 1 that cleaning is effective in improving joint-strength and that of the treatments listed, degreasing in trichlorethylene vapour, followed by a chromic acid pickle, appeared to give the best results.

Other surface treatments were then examined, but the strength of all joints of this set, which included controls degreased and pickled as above, was only of the order of 300 lb.

It was clear that the strength of this set of joints had been affected by some factor as yet uncontrolled. The effect of different factors in the preparation of joints was therefore examined, as described in the following paragraphs.

The glue syrup used for these experiments contained nominally 50% polyvinyl acetate emulsion. The metal strips were cleaned by degreasing and treatment in chromic acid pickle.

(a) Viscosity of Syrup

As no strict attention had been paid to the quantity of methanol used as diluent in the glue syrup, it was thought that it might have some bearing on the final results. Table 2, however, shows that over a much wider range than could have occurred in practice, the quantity of methanol had little or no effect on the failing strength of joints.

TABLE 2. EFFECT OF VARIATION IN VISCOSITY OF SYRUP ON JOINT-STRENGTH

% Methanol	Failing load (lb.)	Mean (lb.)	Remarks
0 (cream)	770, 765, 810, 785	782	All joints displayed adhesion-cohesion failure.
12 (rubbery paste)	670, 845, 865, 810	798	
50 (syrup)	765, 850, 885, —	833	
65 (thin syrup)	655, 880, 800, 750	771	

For ease of spreading it is desirable to have about 50% alcohol present, i.e. sufficient to give a smooth clear syrup.

(b) Atmospheric Conditions at Time of Fabrication

It has been reported that the temperature and humidity of the atmosphere may be critical factors during the application of certain commercial glues for metal. Experimental results appear to show that local cooling, produced by rapid evaporation of solvent in a hot and humid atmosphere, causes deposition of moisture on the spread glue which suffers in joint-strength as a consequence.

Table 3 shows R./4. glue to be independent of temperature or humidity conditions during fabrication of joints.

(a)

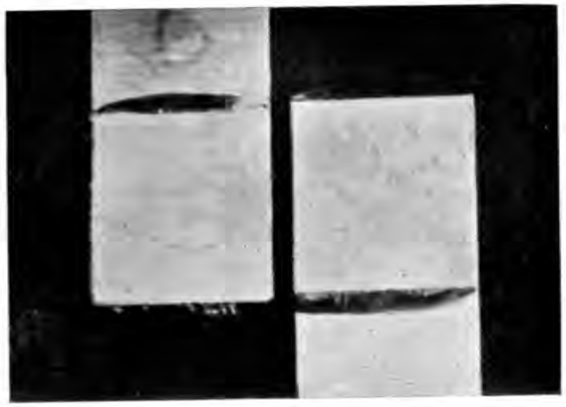
Differential-Strain Failure

Glue has remained attached to the least-strained portions of the metal, i.e. the ends (see Fig. 2).
Magnification x 2.

(b)

Cohesion Failure

Failure has occurred evenly throughout the glue layer, leaving smooth surfaces.
Magnification x 2.



(d)

Dendritic Marking

(This is an extreme example.)
Magnification x 3.

(c)

Adhesion-Cohesion Failure

The glue has failed in patches, leaving a rough surface on each half of the joint.
Magnification x 2.

FIG. 3. APPEARANCE OF BROKEN JOINTS

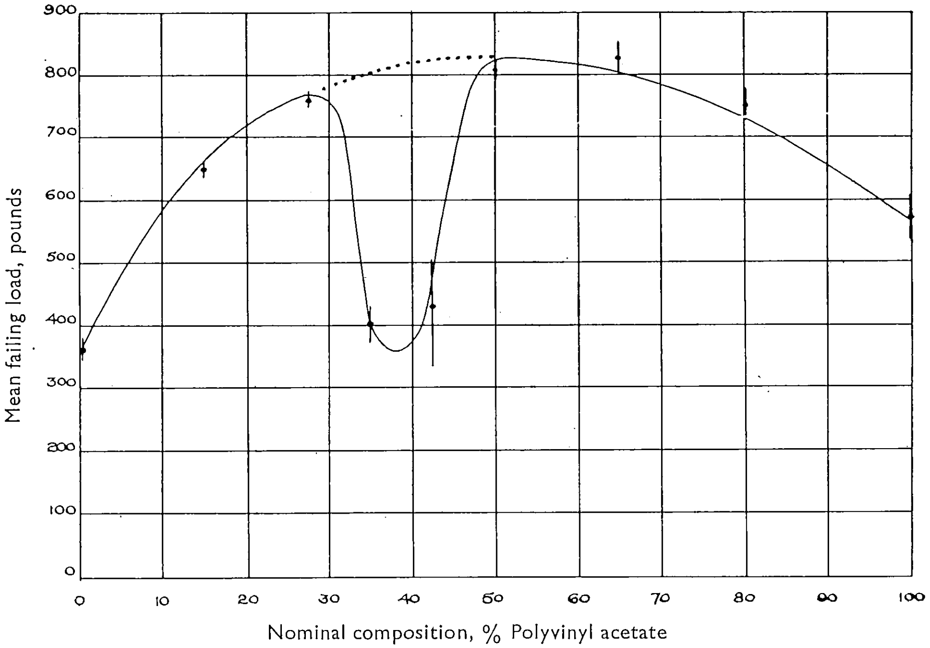


FIG. 4. VARIATION OF JOINT-STRENGTH WITH COMPOSITION OF GLUE

Joints bonded at 105° C. for 20 hours.

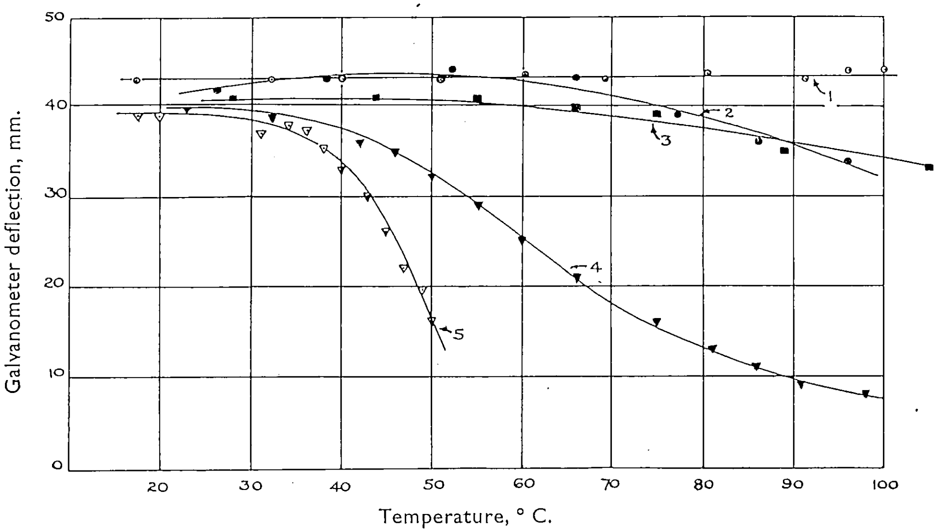


FIG. 5. STRAIN-GAUGE RESULTS, GALVANOMETER DEFLECTION/TEMPERATURE FOR GLUES OF DIFFERENT POLYVINYL ACETATE CONTENT

Ref. 1. No Polyvinyl Acetate
2. 20% ,, ,,
3. 35% ,, ,,
4. 50% ,, ,,
5. 100% ,, ,,

TABLE 3. EFFECT OF VARIATIONS IN ATMOSPHERIC CONDITIONS AT TIME OF APPLICATION OF SYRUP ON JOINT-STRENGTH

Conditions of application and bonding	Failing load (lb.)	Mean (lb.)	Remarks
Laboratory, 21° C., 60% R.H.	810, 880, 840, 860, 805	839	All joints showed cohesion failure with some patches of adhesion failure.
Test room, 36½° C., 18% R.H.	925, 785, 880, 770, 850	842	
Steam-cloud, approx. 36° C. (very wet)	855, 820, 820, 810, 815	824	
Ice-chest, 0-1° C. (wet)	820, 785, 840, 780, 845	814	

(c) Age of Prepared Metal Surface

The surface produced by chromic acid treatment differed considerably in appearance from that of the untreated metal and it was thought that further changes might proceed after removal from the bath and rinsing tank. Table 4, however, shows that joints made at any time within 90 minutes of preparing the surface are unlikely to give much altered results.

TABLE 4. EFFECT OF VARIATION IN TIME INTERVAL BETWEEN PREPARATION OF THE SURFACE AND APPLICATION OF SYRUP ON JOINT-STRENGTH

Interval between preparation and application	Failing load (lb.)	Mean (lb.)	Remarks
Approx. 1 min.	780, 760, 815, 810, 895	812	All joints showed adhesion-cohesion failure
30 min.	950, 960, 850, 915, 945	924	
90 min.	885, 840, 905	877	

Subsequently it has been found that prepared strips, stored free from contamination in a desiccator, may be kept indefinitely without affecting the joint-strength.

(d) Thickness of Glue-line

The glue was applied by brush, and although an effort was made to maintain uniformity in application, it was by no means certain that this was achieved from set to set. Accurate mechanical measurement of the glue-line of cured joints (about 0.001" thick) was difficult and an attempt to obtain it indirectly from the electrical capacitance across the lap-joints was equally unsatisfactory. On the other hand attempts to increase the thickness deliberately resulted only in increased "flash" around the joints, i.e. the extra glue was squeezed out. This is what happened with the various preparations shown in Table 2. Thus large variations in glue thickness are not likely to occur. By diluting the standard mixture, however, and applying approximately equal quantities of solutions of different strength, the thickness could be reduced until the glue became too thin to fill the joint properly. Table 5 shows some results for thin films deliberately obtained in this way, but the joint-strength was not markedly affected.

TABLE 5. EFFECT OF VARIATION OF GLUE-LINE THICKNESS ON JOINT-STRENGTH

Dilution of standard syrup	Failing load (lb.)	Remarks
(undiluted)	745, 785, 695	Cohesion failures, with some adhesion-cohesion and dendritic marking
1 in 2	715, 765, 645*	
1 in 3	635, 720, 540*	

*Imperfectly bonded.

(e) Drying Time

By painting large pieces of aluminium foil with syrup and weighing at intervals, the rate of loss in weight was found to fall rapidly after the first half-hour or so, and to be practically zero after 24 hours, i.e. nearly all the solvent had dried out.

Therefore the normal practice of drying for about 20 hours in a cabinet circulating a large volume of air at 30° C. and 32% R.H., was considered satisfactory, being removed from any critical period.

(f) Bonding Conditions

Joints were always placed in approximately the same position in an oven maintained at 105° C. ± 1° C. The joints were allowed to cool in the oven (switched off, and with the door open) before removal.

The effects of small variations in the time of cure and in the initial rate of cure, i.e. whether the oven was hot or cold to start with (which might affect the loss of volatiles) were investigated. The results are given in Tables 6 and 7.

TABLE 6. EFFECT OF SMALL VARIATIONS IN CURE-TIME ON JOINT-STRENGTH

Time in 105 °C. oven	Failing load (lb.)	Mean (lb.)	Remarks
16 hours	660, 725, 755, 715, 750	721	All joints showed adhesion-cohesion failure
19 ,,	730, 785, 715, 705, 765	740	
20 ,,	730, 720, 795, 760, —	751	
21 ,,	815, 705, 805, 765, —	773	
25 ,,	745, 875, 720, 785, —	781	

TABLE 7. EFFECT OF INITIAL TEMPERATURE OF OVEN ON JOINT-STRENGTH

Initial temperature of oven	Time to attain 105° C.	Failing load (lb.)	Mean (lb.)	Remarks
Room temp.	22½ min.	860, 935, 870, 875, 775	863	All joints showed adhesion-cohesion failure
65° C.	10 ,,	775, 855, 860, 820, 820	826	
105° C.	—	790, 815, 870, 910, 850	847	

It may be concluded that there is nothing critical in the initial rate of cure and the slight upward trend with increase of cure time (Table 6) is of little significance since previous joints had been cured for 20 hours ±1 hour.

(g) Time Interval Between Fabrication of Joint and Testing

Before test, all joints were conditioned for at least 24 hours in the testing room in Engineering Division, N.P.L., which is maintained at 21° C. and 55% R.H. Table 8 gives the strength of joints which had been conditioned for different periods.

TABLE 8. EFFECT OF TIME INTERVAL BETWEEN FABRICATION OF JOINT AND TESTING ON JOINT-STRENGTH

Interval between fabrication and testing	Failing load (lb.)	Mean (lb.)	Remarks
1 hour	840, 725, 810, 735, 800	782	All joints similar in appearance, adhesion-cohesion failures
7 hours	730, 815, 820, 735, 775	775	
5 days	845, 885, 865, 900, 875	874	
Repeat experiment, with another set of joints :			
1½ hours	750, 775, 725, 765	754	
6 days	790, 875, 895, 865	856	

A significant but small increase in strength is observed as the interval between fabrication and testing is increased from 7 hours to 5 days. This observation was confirmed by the repeat experiment, but neither this effect nor any of the other factors investigated in the preceding paragraphs account for the major reduction in strength obtained with the second set of experiments on surface treatment.

A fresh sample of glue was prepared for each set of experiments. The components were weighed, but as only small quantities were involved the composition of the different syrups might easily have varied by ±5%. It did not seem probable that such a small variation in composition would account for a 50% reduction in joint-strength, but it was felt advisable to examine this factor.

VI. Effect of Variations in Composition of Syrup on Joint-Strength

Throughout this report, the composition of a syrup is based on the relative proportions of the two main components, i.e. the vinyl emulsion and the phenolic solution. Thus a syrup containing nominally 50% PVAc was made by mixing equal parts by weight of the vinyl emulsion and the phenolic solution. The vinyl emulsion contained 56% polyvinyl acetate, whilst the phenolic solution contained 52% of resin-forming material. The estimated true composition of cured glue-films derived from syrups of different composition is given in Appendix 1.

In Table 9 are given the strengths of joints made from syrups accurately prepared and containing from 0 to 100% of vinyl resin.

TABLE 9. EFFECT OF COMPOSITION OF SYRUP ON JOINT-STRENGTH

% Vinyl resin in glue	Failing load (lb.)	Mean (lb.)	Percentage standard error of mean*	Appearance of broken joints
0	405, 380, 315, 365, 335	360	4%	Thin films, adhesion-cohesion failures
20	695, 750, 710, 730, 700	717	1%	,, ,, with dendritic markings
35	375, 440, 360, 490, 590	451	9%	Thin, dendritic, well-defined differential effects
50	830, 730, 725, 770, 835	778	3%	Adhesion-cohesion failures
65	795, 800, 905, 800, —	825	3%	,, with tendency to adhesion failure
80	655, 790, 730, 745, —	730	4%	Adhesion failures
100	510, 515, 510, 725, 595	571	7%	Thin, patchy, ill-defined type of bonding

$$\text{*Standard error of the arithmetic mean} = \frac{\text{standard deviation of a set of observations}}{\sqrt{\text{no. of observations in the set}}}$$

It will be observed that mixes of the two resins give stronger joints than either of the resins by themselves, but that a syrup containing 35% vinyl resin gives anomalous low results. The critical range of composition, 15-50% vinyl resin, was therefore examined in greater detail. (See Table 10.)

TABLE 10. STRENGTH OF JOINTS FROM SYRUPS OF CRITICAL COMPOSITION

% Vinyl resin in glue	Failing load (lb.)	Mean (lb.)	Standard error of mean	Appearance of broken joints
15	680, 640, 620, 645, —	646	2%	Thin films, adhesion-cohesion failures, slight differential strain
20	760, 670, 735, 685, 745	719	2%	"
27½	760, 725, 745, 775, 785	758	1%	"
35	360, 360, 365, 380, 260	345	6%	Thin, dendritic, part adhesion - part differential failures
42½	650, 275, 385, 400, —	428	18%	"
50	815, 865, 805, 850, 845	836	1%	Adhesion-cohesion failures, partly dendritic

The above results are in excellent agreement with those of the previous table; syrups containing 35 and 42½% vinyl resin give low and erratic joint-strengths.

As a final check on the above abnormal result, joints were made from fresh syrups containing 20, 35 and 50% vinyl resin. In addition, the 20 and 50% syrups were mixed in the correct proportion to yield a 35% syrup. Two sets of 35% joints were thus available. The results of this experiment are given in Table 11.

TABLE 11. JOINT-STRENGTHS FROM 35% SYRUP OBTAINED BY MIXING 20 AND 50% SYRUPS

% Vinyl resin in glue	Failing load (lb.)	Mean (lb.)	Standard error of mean	Appearance of broken joints
20	715, 675, 665, 665, 710	686	2%	Thin films, adhesion-cohesion failures
35A	290, 250, 270, 370, 265	289	7%	Dendritic, adhesion failures with differential effects
35B	290, 300, 285, 300, 255	286	4%	
50	770, 785, 820, 640, 685	740	4%	Adhesion-cohesion failures

A=Prepared directly. B=Prepared by mixing 20 and 50% syrups.

These experiments are conclusive; there can be no doubt that the 35% polyvinyl acetate lap-joints give much lower strengths than the 20 or 50% joints made under the same conditions. The reason for the anomaly is obscure. Addition of phenolic resin to polyvinyl acetate may be expected to increase joint-strength simply by increasing the cohesive strength of the vinyl resin. Again, increase in joint-strength resulting from addition of polyvinyl acetate to phenolic resin is explicable on the grounds that the vinyl resin acts as a plasticizer and relieves stress concentration in the phenolic resin which by itself is very brittle. Hence, joint-strength might be expected to vary with composition in the manner indicated by the dotted line in Fig. 4. In practice, the 35% and 40% lap-joints possess much reduced strength. (See also Section VII (f) on butt-joints.)

It is quite clear that the composition of the syrup is critical and that a small error in making up the syrup for 50% vinyl resin glue might well have been responsible for the low results obtained in Section V.

VII. Effect of Variations in Composition on Other Properties of the Glue

In this section are described experiments which were undertaken in an attempt to reveal the cause of the anomaly described above. On examination after failure, joints from the 35% syrup almost invariably showed differential strain, but apart from this effect they did not appear different from those made from compositions giving joints of higher strength.

(a) Density

It was not found possible to determine the density of the glue film within a joint, but an estimate was made by determining the density of films baked on to thin aluminium foil, the syrups and conditions of drying and baking being similar to those used in the preparation of joints. The densities of films obtained from syrups containing 20 and 50% PVAc were 1.278 ± 0.002 and 1.247 ± 0.002 gm. per c.c. respectively. On the basis of a simple mixture law a syrup containing 35% PVAc should give a film of mean density 1.262 gm./c.c. The experimental value obtained was 1.262 ± 0.002 gm./c.c. which suggests that the 35% resin prepared in this way is not anomalous with regard to density.

(b) Resistance to Solvents

Cured films of the three different compositions were practically unaffected by immersion for some time in water or petrol. Alcohol, benzene and acetone had no apparent effect upon 20% films and the 35% resin was very little altered, but the 50% films, especially with acetone, soon softened, swelled and eventually broke up into small rubber-like particles. The 20% resin was resistant to boiling in acetone, but the 35% film was slowly softened by this treatment. The behaviour of the 35% film to solvents was therefore quite normal.

(c) Softening Range

The N.P.L. resistance strain-gauge can be used to provide a measure of the softening range of a glue. A gauge is stuck to a metal bar by means of the glue under examination. When the glue has set, strain given to the metal bar is transmitted through the glue to the gauge and may be observed as a galvanometer deflection. But if the gauge and bar are heated to the softening temperature of the glue, the glue ceases to transmit strain from bar to gauge and the galvanometer deflection falls to zero. From a plot of galvanometer deflection against temperature, the softening range of the glue may be estimated.

Fig. 5 gives the results of such a determination on glues containing 0, 20, 35, 50 and 100% polyvinyl acetate. In general, an increase in phenolic content increases the thermal stability of the glue; there is little difference between the thermal stabilities of the 20 and 35% glues which are both superior to the 50% glue. The technique is not sufficiently sensitive to decide whether the 35% resin is anomalous.

(d) Joint-strength at High and Low Temperatures

The strength of joints at high and low temperatures was obtained by surrounding the specimens in the testing machine with a heater and freezing-box respectively. The results of such tests, together with controls at room-temperature, are given in Table 12 and Fig. 6.

TABLE 12. JOINT-STRENGTH AT HIGH AND LOW TEMPERATURES

Temperature of test (°C.)	% Vinyl resin and Failing load (lb.)					
	20%	Mean	35%	Mean	50%	Mean
+21	555,555,510	540	415,380,305	366	730,750,715	732
−23	605,715,595	638	245,245,255	248	535,485,585	535
+21	660,710,625	665	310,280, —	295	880,865,870	872
+100	685,545,600	610	535,385,365	428	265,275,245	262

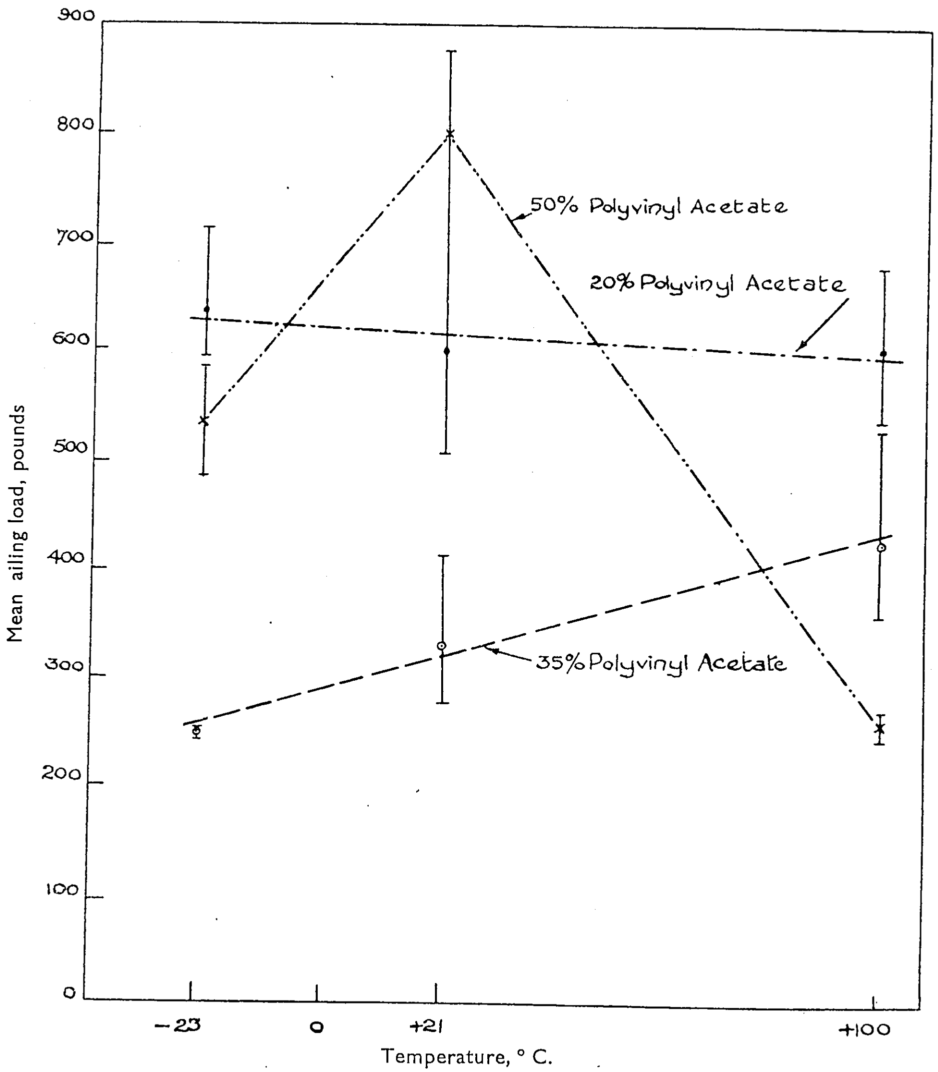


FIG. 6. COMPARISON OF JOINT-STRENGTH AT 3 TEMPERATURES, FOR 3 DIFFERENT COMPOSITIONS OF GLUE

Lines extending above and below mean values (shown by °, etc.) indicate maximum scatter of results.

Type of Failure. 20%, all cohesion. 35%, 21° C., all differential; —23° C. central area, cohesion, outer margin, adhesion; +100° C., cohesion. 50%, all cohesion or adhesion-cohesion.

The results are consistent with the softening range experiments. The 20 and 35% resins are not greatly affected by the temperature of test, but due to increase in the proportion of linear polymer, joints from 50% resin tested at 100° C. show much reduced strength. The latter glue also gives joints with reduced strength at —23° C., possibly due to embrittlement of the polyvinyl acetate component.

These tests provide no clue to the anomalous behaviour of the 35% vinyl resin.

(e) Mechanical Properties of Mouldings and Films

A possible reason for the low strengths given by the 35% vinyl resin in lap-joints was that the glue film itself possessed reduced strength or low extensibility.

Two attempts were made to determine the mechanical properties of resins of different composition. In the first, syrups containing 20, 35 and 50% vinyl resin were spread on glass plates and allowed to dry. The tacky film was then removed and moulded into tensile test-pieces (1½″ long, ¼″ thick, ¼″ wide in the waisted portion). The production of the film, followed by the moulding (20 hours at 105° C. at 50 lb./sq. in.) approximated to the conditions of joint fabrication.

Several specimens of each composition were made, but owing to the low pressure employed it was not possible to obtain entirely void-free mouldings. The test-pieces were pulled in tension, the ultimate tensile strength and breaking elongation being noted. The 20 and 35% test-pieces behaved similarly, each had a tensile strength of about 4,000 lb./sq. in. and a breaking elongation of about 2%. The 50% mouldings were very much less stiff, the breaking extension was of the order of 100% and the tensile strength about 2,500 lb./sq. in.

The above test-piece could not be considered satisfactory in that the resin was in the form of a massive moulding whilst in the actual lap-joint the resin film is about 0.001″ thick. An attempt was therefore made to examine the breaking-elongation of thin films using the "stress-coat" principle. Flat strips of 20 gauge duralumin ½″ × 10″, were thinly coated over their central portion with syrups of different composition. The films were allowed to dry and then baked at 105° C. for 20 hours.

The duralumin strips were pulled in a tensile testing machine and the load noted at which the first crack appeared in the resin film. Knowing the Young's modulus of the duralumin, it was hoped by this means to estimate the breaking-strain of the resin film. By this test a film of phenolic resin, containing no polyvinyl acetate, gave a breaking strain of 2-4%. Unfortunately, the method could not be used for films containing polyvinyl acetate because the breaking strain exceeded the yield value of the duralumin. All that can be said is that resin films containing 15% or more PVAc had a breaking strain in excess of 5% and that the 35% composition appeared to be at least as extensible as the 20% resin.

Both experiments on the mechanical properties of resins were inconclusive, but no evidence of anomalous behaviour by the 35% composition was obtained.

(f) Butt-joints

Further evidence of normal behaviour of the 35% glue has recently been obtained from tensile tests on butt-glued duralumin bars (i.e. glued end to end, instead of the usual lap-joints). On testing these joints the glue was subjected to approximately pure tension at right angles to the plane of the film. The jig used for holding the butt-joints in compression during cure was, however, not entirely satisfactory and needs re-designing before extensive investigations are made, but the results available indicate that surprisingly high strengths can be attained.

The 20% vinyl-resin glue, on butt-joints 1″ × 0.2″ in area, gave a mean failing value of 2,650 lb. (equivalent to approximately 6 tons/sq. in.). 50% glue gave considerably lower results and those for 35% resin lay approximately between the other two. Thus there is apparently no marked anomaly with butt-joints from 35% vinyl-resin glue when made and cured under the same conditions as those which provide low values with lap-joints. The significance of these results is discussed in Section IX.

VIII. The Effect of Variations in the Conditions of Bonding

The results described in the previous sections were obtained on joints which had been bonded at 105° C. for 20 hours, and it has been shown that small variations in the bonding-time have little effect on the strength of joints made from resin containing 50% PVAc (see Table 6, Section V (f)). It seemed possible that the low results given by the 35% composition might be due to bonding under conditions which were not optimum. In this section the effect is described of bonding at different temperatures for different times.

In Fig. 7 it will be seen that over a wide range of bonding times low results are given by the 35% resin at both 105° C. and 75° C. Suitable times for bonding at 75° C. were estimated on the hypothesis that the rate of cure of the phenolic resin would be halved for a drop in temperature of 10° C. This hypothesis, which was supported by the experimental results, was again used to estimate suitable bonding times for cure at 115° C. and 130° C. The results of these investigations are summarised in Table 13.

TABLE 13. STRENGTH OF JOINTS BONDED AT DIFFERENT TEMPERATURES

Bonding temp.	Bonding time	20% PVAc Individual results (lb.)	20% PVAc Mean	35% PVAc Individual results (lb.)	35% PVAc Mean	50% PVAc Individual results (lb.)	50% PVAc Mean
75° C.	150 hr.	640,620,615	625	360,225,225	270	785,760,820	788
105° C.	20 hr.	680,635,595	637	325,290,270	295	805,825,840	823
115° C.	10 hr.	720,705,705	710	440,400,310	383	775,820,915	837
130° C.	3¾ hr.	670,655,605	643	400,325,315	347	605,685,640	643

The reproducibility of the above results is satisfactory and it will be noted that the joints containing 35% PVAc were consistently lower in strength than those of the other compositions at the four temperatures of bonding examined. Joints prepared from 50% PVAc are significantly lower in strength when bonded at 130° C. compared with those bonded at the lower temperatures.

Bonding at 145° C. was next examined; all joints bonded at this temperature gave conflicting and irreproducible results. From the first set of results, it appeared that the 35% resin gave *higher* joint strengths than either the 20% or 50% resin. Repeat tests failed to confirm this result and the values available at present are too erratic to be of much significance. The following tentative conclusions are made on tests at 145° C.

(a) The reproducibility of joints bonded at 145° C. is inferior to that obtaining at lower temperatures.
(b) Joints made with glue containing 35% PVAc appear to give *higher* strengths, when bonded at 145° C., than at lower temperatures.
(c) Joints made with glue containing 20% and 50% PVAc appear to give *lower* strengths, when bonded at 145° C., than at lower temperatures.

Examination of the broken test-pieces failed to reveal any clue to these conflicting results. Further work is required before it would be wise to speculate on explanations for the critical behaviour at 145° C.

IX. Conclusions and Future Work

Conclusions which may be drawn from this preliminary study of factors affecting the strength of glued joints in duralumin are as follows :—

1. Bonding temperature has a marked effect on the strength of joints made with R./4. glues. The results obtained with lap-joints bonded at 130° C. (and below) were in general reproducible, but irregular and lower strength was obtained from joints bonded at 145° C.

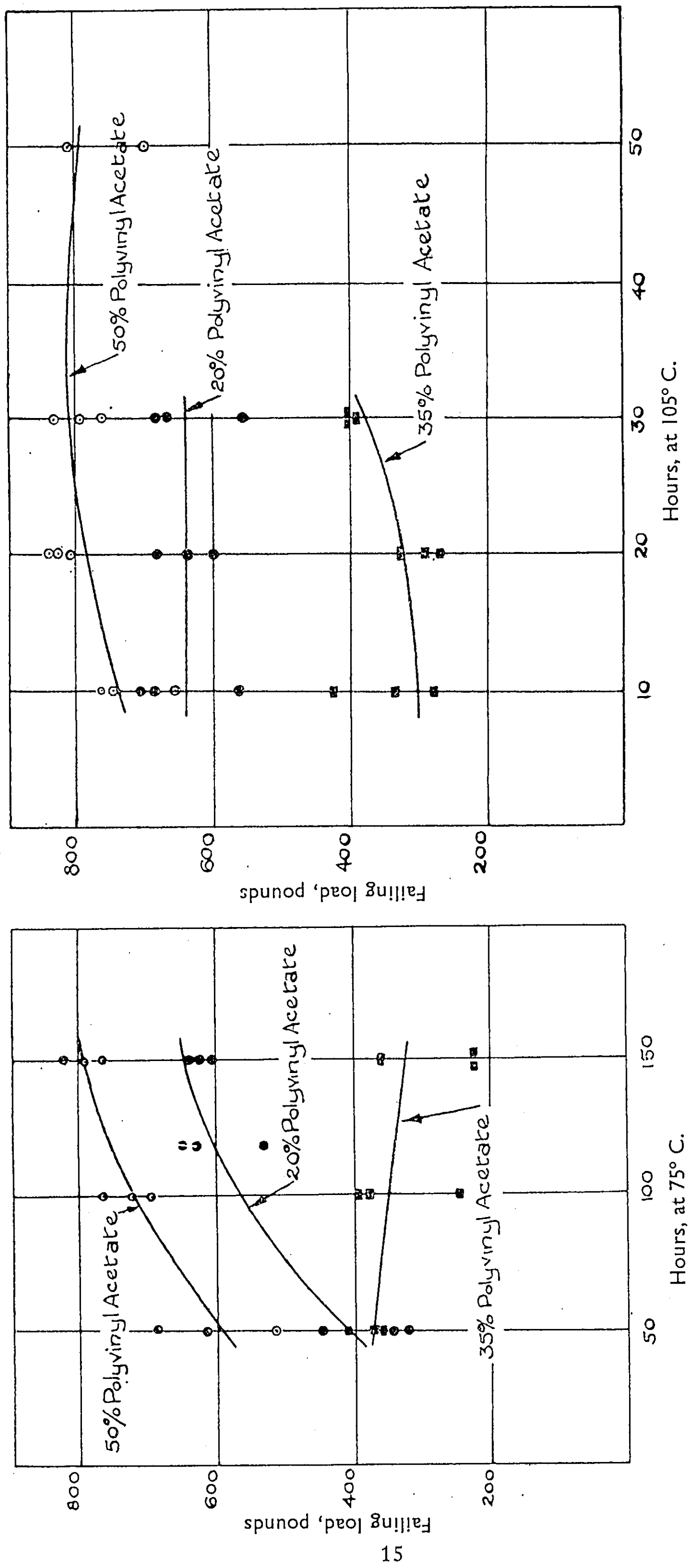


FIG. 7. RELATIONSHIP BETWEEN STRENGTH OF JOINTS AND TIME OF BONDING, (A) AT 75° C., (B) AT 105° C.

It should be emphasised that the effect of the bonding temperature has so far been observed only with the mixture of polyvinyl acetate emulsion and phenolic resin, but if other mixtures of linear and cross-linking polymers exhibit the same inconsistent behaviour the effect is of practical importance.

2. When cured at 130° C. (or below), glues containing 30-45% polyvinyl acetate gave anomalous low strength with lap-joints.

This effect has been observed at a number of bonding temperatures and also when the vinyl emulsion in R./4. syrup was replaced by solutions of two commercial vinyl derivatives. It is unlikely that reduction in joint-strength of the 35% vinyl resin glue derives from reduced specific adhesion since the effect was not observed in butt-joints, where the glue was subjected mainly to direct tensile stress. The physical properties of films and mouldings from the 35% glue were normal and intermediate between those for the 20% and 50% mixtures. The only physical difference observed was the much more frequent occurrence of differential strain failure in the 35% lap-joints.

It would appear at first sight that the 35% vinyl-resin glue, although normal in tension, is anomalously weak in shear. In practice, however, these two properties are usually closely related and a more probable explanation lies in the fact that in tests on lap-joints considerable tearing stresses are involved (as mentioned in Section III). However, an explanation of this anomaly must await more precise and detailed examination of the properties of cured films and mouldings of varied composition; all that can be said at present is that the 35% glue appears to possess exceptionally low resistance to tearing stresses.

3. Apart from the instances of critical composition and maximum temperature of cure, as cited above, polyvinyl acetate-phenolic resin mixtures have been shown to be tolerant to variations in conditions of joint-fabrications.

This conclusion derives from the comparative uniformity of results in the various tests described in Section V *et seq.* The values for failing loads were shown to be relatively independent of the viscosity of the syrup or the atmospheric conditions at the time of its application. They were almost unaltered by likely variations in the thickness of syrup applied, in the age of the prepared surface or in the drying time used, and were but little affected by small changes in the bonding conditions or the interval between bonding and testing.

ACKNOWLEDGMENTS

The authors wish to thank Dr. F. T. Barwell of Engineering Division, National Physical Laboratory, for advice and suggestions and also to acknowledge the assistance rendered by Miss P. E. Turner of Engineering Division, N.P.L., who performed most of the tests on joint-strength described in this report.

X. Appendices

Appendix 1

Standard Procedure Adopted in Making Test-joints with R./4. Glue

1. Preparation of the glue.
2. Preparation of the metal.
3. Fabrication of the joints.

1. Preparation of the Glue

The polyvinyl acetate was originally used in the form of a commercial emulsion containing 56% solids and the phenolic resin was a commercial aqueous solution of about 52% solid content. The glue was based on the direct ratio of these two components, thus "50% vinyl-resin" meant 50% by weight of the emulsion in an intimate mixture of emulsion and phenolic solution. The mix so prepared was stirred and diluted with methanol until of a brushing consistency; it was left for air-bubbles to disperse and was then ready for use.

The following table gives the nominal compositions of the three principal syrups discussed in the Report, with an indication of the solids ratio (on the basis of 56% vinyl solids and 52% phenolic solids in the respective initial components).

COMPOSITIONS OF THE THREE PRINCIPAL R./4. GLUE SYRUPS

Nominal % vinyl-resin in glue	Typical composition of syrup for brushing consistency (parts by weight)			Actual % vinyl-resin* in glue
	Vinyl emulsion	PF resin solution	Methanol	
20	20	80	Approx. 70	21
35	35	65	,, 95	36.5
50	50	50	,, 105	52

*On the basis of 56% vinyl solids and 52% phenolic solids.

2. Preparation of the Metal

The metal pieces were cut from stock sheet and milled to size. To ensure as much uniformity as possible each strip was inspected and very lightly stoned to remove burrs, etc., but relatively few had to be rejected for major defects. A gauge-line was scribed ½″ from each end to determine the length of overlap.

They were then swabbed with cotton-wool soaked in acetone, space-stacked in a wire cage and degreased in refluxing trichlorethylene vapour for at least 10 min. The strips were then removed, cooled, and the ends immersed to a depth of about 1″ in D.T.D. 915A chromic acid pickle; the bath was kept at 55-60° C. and treatment lasted 20 mins.

The strips were then freely washed in running cold water, rinsed in distilled water, and blotted dry with clean filter paper. They were then stored in a desiccator, ready for use.

3. Fabrication of the Joints

The syrup was applied evenly with a small brush to the strips which were then laid horizontally and left overnight in a cabinet at 30° C. 32% R.H. Next day the strips were pressed tightly together by hand, in the form of lap-joints, and finally secured with spring paper-clips to keep them in contact.

After 20 hours in an oven at 105° C. the joints were allowed to cool, the clips were removed and any excessive "flash" was filed off. The joints were tested after an interval of 2 to 3 days.

Appendix 2

Reproducibility in Strength of Joints

1. Reproducibility Within a Single Set

A set of 20 joints was made according to the standard recipe described in Appendix 1. All the metal strips were degreased and pickled together and after applying the glue syrup, the coated strips were dried and finally bonded as a single batch. The joints were then tested at C.R.L., in a Denison tensile testing machine, using a constant rate of loading of 1,000 lb. per minute. The results are as follows:

Reproducibility of Results within a Single Set

770; 770; 770; 800; 790;
795; 780; 810; 800; 775;
750; 685; 780; 775; 750;
730; 760; 790; 780; 800;
} *Failing load in lb.*

Mean Failing Load = 773 lb.
Standard Error of Mean = 1%

2. Reproducibility from Set to Set

From one sample of R./4.50 glue syrup, five sets of joints were made at different times, over a period of 16 weeks. Each set, which consisted of 5 individual joints, was tested by the Engineering Division, N.P.L. The results are given in the following table:

REPRODUCIBILITY OF RESULTS OVER A PERIOD OF 16 WEEKS

Age of glue syrup	Failing load (lb.)	Mean (lb.)	Standard error of mean
0 weeks	830, 730, 725, 770, 835	778	3%
1 week	825, 715, 840, 860, 855	819	3%
4 weeks	810, 900, 855, 895, 810	854	2%
8 weeks	780, 790, 815, 635, 775	759	4%
16 weeks	880, 740, 940, 875, 850	857	4%

Failing load, grand mean = 813 *lb.*
Standard error of grand mean = 2%

Appendix 3

Strength of Alclad Joints: Results for R.A.E.-Type Joints

The test-pieces used for the work described in the Report were of duralumin, but Alclad would more probably be employed in practice because of its greater corrosion resistance. The strength of R./4.50 joints in duralumin and in Alclad was compared using the C.R.L. test-piece (½″ × ½″ × 0.1″) and also the R.A.E. test-piece (½″ × 1″ × 20 gauge), comparison of the two types of joint being also obtained. The results are as follows:

COMPARISON OF JOINT-STRENGTH IN DURALUMIN AND ALCLAD WITH R./4.50 GLUE

Test-piece	Material	Failing load (lb.)	Mean (lb.)
C.R.L.	Alclad	755, 755, 725, 770, 755	752
C.R.L.	Duralumin	810, 750, 765, 815, 770	782
R.A.E.	Alclad	1160, 1270, 1245, 1140, 1280	1219
R.A.E.	Duralumin	1325, 1220, 1290, 1195, 1330	1272

With either test-piece, the difference between the means for Alclad and duralumin is without appreciable significance.

Report No. 2

Adhesion of Glues to Plywood (Part I)

(Based on R.A.E. Report MAT/N/1/2001, September, 1941)
by Dr. M. G. M. Pryor

U.D.C. No. 668.3 : 674-419

Abstract

The factors affecting the adhesion of casein and synthetic resin glues to plywood are reviewed, and the nature and the occurrence of the so-called case-hardening of plywood are discussed. The information collected about the occurrence of case-hardening in plywood and veneers does not agree with previous theories about the nature of case-hardening; an alternative theory depending on the crushing of the plywood during manufacture is put forward, and remedies for case-hardening are discussed. Case-hardening cannot be avoided in thin plywood, but it can be cured by rubbing the glue into the wood before assembly, or by removing the surface layers of the wood with sandpaper. As a result of the investigation, it is recommended that all plywood should be sandpapered before gluing.

Contents

Illustrations

I. Introduction

It has been known for some time that the adhesion of glues to plywood, particularly to thin plywood, is often very weak. The attention of the R.A.E. was first drawn to the matter by Dr. de Bruyne, of Messrs. Aero Research Ltd., in October, 1938.

In the instance described by Dr. de Bruyne [1] some thin plywood (to specification 4.V.3) which formed part of the skin covering of a tailplane had dropped off the ribs while the parts were in store. The adhesive used was a urea-formaldehyde resin ; the adhesive itself did not seem to be at fault, so that it appeared that the failure must be due to some defect in the plywood. Further investigation established the following points :

(1) The effect was confined to the surface of the plywood ; it was destroyed by sandpapering the surface.
(2) It was most common in thin plywood (up to about 1 mm. thick).
(3) The condition could be alleviated by dipping the plywood in boiling water after pressing.
(4) No difference could be detected in the appearance under a microscope of affected and normal plywood.

On the strength of these results, de Bruyne proposed a theory to account for the failure of glues to adhere to plywood affected in this way. This theory may be summarized as follows. The specific adhesion of glues to wood is due to the formation of ionic bonds between polar groups in the glue and similar groups in the wood, of which the most important are the hydroxyl groups of the cellulose. At normal humidities these groups are strongly hydrated, but if the wood is strongly heated or dried the bound water is driven off, and the hydroxyl groups of neighbouring chains condense with each other to form ether linkages, which are not easily hydrolysed when the cellulose is once more exposed to water.

This "cellulose anhydride" might be expected to be less reactive than normal cellulose, and in particular, to show less affinity for glue. This theory was elaborated in an article in *Flight*[1] published in 1939. In this article, a form of test is described, elaborated by Kohman (1939),[2] by means of which it is claimed that the decrease in the affinity of overheated plywood for water can be demonstrated. In this test thin strips of material are made to project through a benzene/water interface. If the contact angle of the surface is less for benzene than it is for water, the meniscus will bend down into the water (b, Fig. 1) and vice versa. It is claimed that this test will differentiate between normal and overheated plywood ; with normal wood the meniscus bends up ; with overheated wood, down (see Fig. 1).

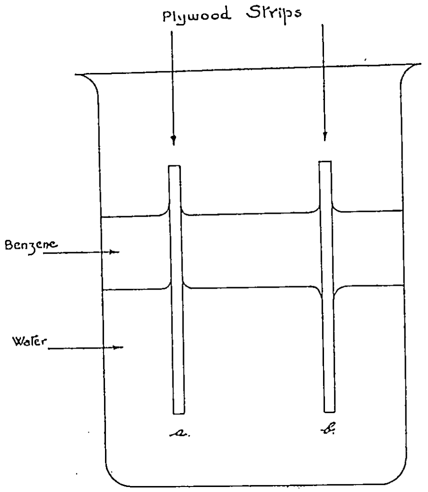


Fig. 1. INTERFACE TEST

Later work at the R.A.E. did not confirm the value of this test ; with some samples of plywood the meniscus did bend downward, but these samples did not necessarily show bad adhesion.

After the publication of de Bruyne's article, the problem was investigated at the R.A.E., but no definite conclusions were reached. Strength tests used to detect case-hardening were found to give results with a wide scatter, and no consistent difference could be found between plywood which had been treated so as to make it case-hardened and plywood which was assumed to be normal. Later work has shown that the most probable explanation of this failure was that all the supposedly normal plywood used as a control was to some extent case-hardened. It has also been found that joints which give reasonable strength when tested in shear, show up very badly in a handling test in which the loading is mainly tension. This was not realized at the time, however ; the results obtained were not thought to be worth publication, and the investigation was temporarily abandoned.

At the same time, acting on the assumption that the cause of the trouble was, in fact, dehydration of the cellulose due to overheating, regulations were made governing the manufacture of plywood to B.S. 5.V.3, which were designed to eliminate the causes of case-hardening. It was laid down that the plywood should never come into direct contact with the heated platens of the press, but should always be separated from them by plywood boards or thick veneers. Firms were encouraged to restore the water content of their plywood after it had been pressed by dipping it in water, a practice which was already almost universal.

II. Tests used to Detect "Case-Hardening"

The test specimen originally used at the R.A.E. to detect case-hardening in plywood consisted of a 1″ square of plywood inserted in the overlap of a standard walnut lap-joint test piece to B.S. 3.V.2. This form of test will be referred to as the "old sandwich test." It has two disadvantages : (a) the two sides of a piece of plywood cannot be tested separately, and (b) errors may arise from the fact that the adhesion is sometimes better near the edges than it is in the middle.

These disadvantages were overcome by using a modified form of the test piece, in which a strip of plywood a little longer than one of the walnut slips is used, instead of a square. The strip is glued to one of the walnut slips so that it completely covers one face of the walnut, and projects about $\frac{1}{4}$″ at one end (see Fig. 2). The test piece is then assembled in the usual way, so as to give an overlap

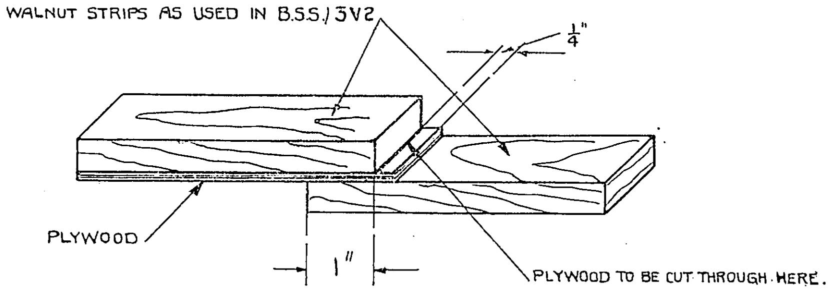


Fig. 2. MODIFIED SANDWICH TEST

of 1″ (reckoned from the end of the walnut) at the end at which the plywood projects. When the glue has set, the projecting part of the plywood is cut through and the glue fillets are trimmed off at the ends and sides. This test piece is convenient to use, although it is troublesome to make. It will be referred to as the "modified sandwich" test.

The way in which the sandwich and the modified sandwich test pieces are assembled is not at all like the conditions under which joints involving plywood are made in practice. A third type of test piece was used therefore, in which the joint could be made up under more typical conditions; this was called the strip test (see Fig. 3). Strips of plywood one inch wide are glued to a flat spruce board, so that they project one inch over the edge. The spruce board is then clamped to a plate which can be fixed to a stand at a known angle to the vertical, and the strips are peeled off by a load applied at the end. Load was applied by pouring lead shot into a container suspended by a string from a hole near the edge of the projecting part of the strip. This test piece only yields useful results with fairly thick plywood; if the strips are less than about $1\frac{1}{2}$ mm. thick, the plywood fails in bending.

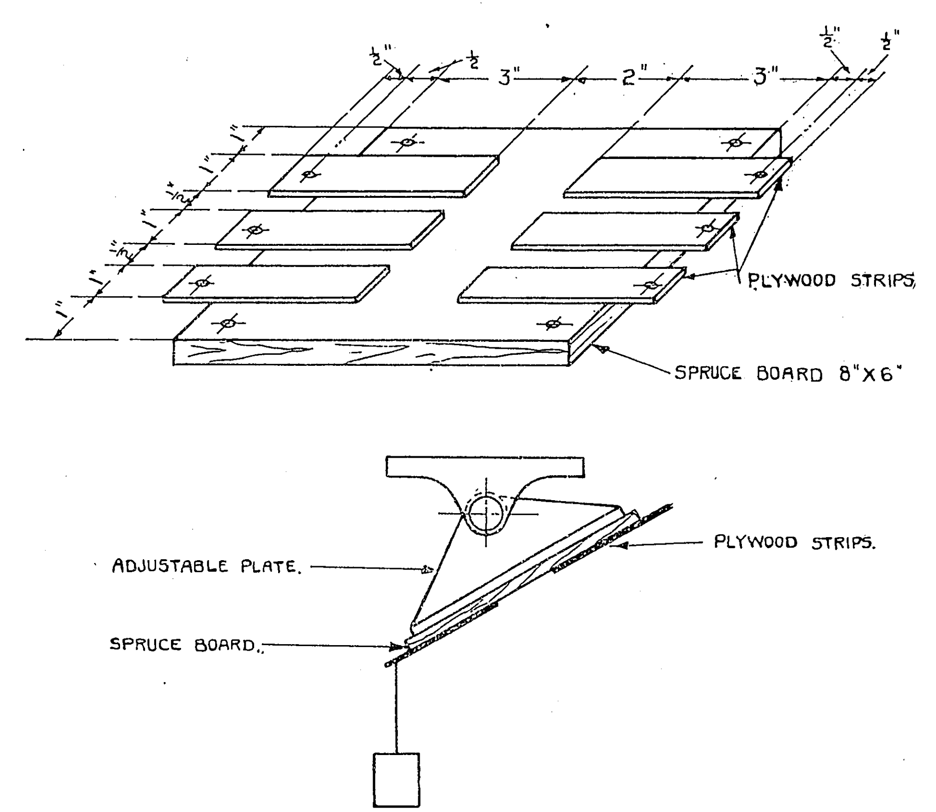


FIG. 3. STRIP TEST

This specimen takes a long time to test; for preliminary tests a rough peeling test was used in which strips of plywood were glued to a narrow spruce block and pushed off by hand. The appearance of the broken surface was found to be a good guide to the strength of the joint; this was confirmed by an inspection of the broken surfaces obtained in more careful tests. Joints made with normal plywood usually fail in such a way as to leave a covering of wood fibres or even complete veneers, adhering to the glue. Joints made with case-hardened plywood, on the other hand, always fail at the junction of the plywood and the layer of glue; the plywood peels off entirely, leaving exposed a clean layer of hardened glue, which bears on its surface a cast of the surface of the plywood. This type of failure was assumed to be diagnostic of case-hardening. The difference between normal and case-hardened plywood was much more noticeable in this test than in the quantitative shear and peeling tests.

For most of these tests Beetle Cement 'A' was used, because it is more sensitive to case-hardening than is casein. The joints were made up under very low pressures, so that the glue line was between 10-50/1000″ thick, because it was felt that this was more like commercial practice than the standard test procedure, in which a pressure of 200 lb./sq. in. is applied.

III. Preliminary Experiments

By the use of the rough peeling test it was found that nearly all plywood to specification 5.V.3, less than about $1\frac{1}{2}$ mm. thick, is case-hardened to some extent. The degree of case-hardening varies; a few samples show good adhesion, and all degrees of transition are found between these and the completely case-hardened type. The frequency of occurrence and degree of severity decreases with increasing thickness of the plywood; 1 mm. plywood is nearly all severely case-hardened; 1.5 mm. is mostly case-hardened; 2 mm. plywood usually shows good adhesion. Severe case-hardening does occur in thick plywood, however. It has been found in samples of 3-ply 3 mm. thick and of 5-ply 4 mm. thick.

The same conclusions apply to plywood (D.T.D. 427) bonded with urea-formaldehyde resin, although this is not subjected to such a high temperature or pressure during manufacture. No data were available on plywood bonded with casein or blood albumen.

An investigation was also made of samples of birch veneers, and it was found that they often show typical case-hardening. Heart-wood veneers were more often affected than sap-wood, and those in which the grain made a steep angle to the surface than those in which it ran parallel.

As well as investigating the incidence of case-hardening in veneers as supplied by plywood manufacturers, an attempt was made to make normal veneers case-hardened by various experimental treatments. Canadian birch veneers $\frac{1}{16}$″ thick were used for these experiments. Sap-wood veneers in which the grain was more or less parallel to the surface could not be rendered case-hardened by any treatment; if they were pressed at 400 lb./sq. in. between steel platens heated to a temperature of 200° C. for five minutes, they acquired a high gloss, but even then they did not lose their gluing properties. The following combinations of pressure and temperature were tried: 50, 100, 200, 400, 600, 800, 1,000, 2,000 lb./sq. in. cold; 50, 200, 300, 400 lb./sq. in. at 150° C. and at 200° C. All these treatments were without effect.

For experiments on the case-hardening of heart-wood veneers, a sample of veneer which is not case-hardened to start with is necessary. This is difficult to obtain, probably because most firms use patent veneer drying machines in which the veneers are dried and flattened between hot metal plates, so that any veneer which is susceptible has an opportunity of becoming case-hardened. Some kiln-dried heart-wood veneers which were not initially case-hardened were, however, obtained from the Forest Products Research Laboratory and these were subjected to similar treatment to that given to the sap-wood veneers. Almost any combination of a high temperature (150-200° C.) and pressure (5-500 lb./sq. in.)

was effective in case-hardening the veneers. Pressures between 50 and 1,600 lb./sq. in. applied cold were also effective. In a series of veneers pressed cold at various pressures, there was some evidence that very high pressures (3,000-12,000 lb./ sq. in.) did not case-harden the veneers as efficiently as lower pressures, but these results could not be repeated. A high temperature without any pressure had no effect. Veneers heated in an oven at 200° C. for 5 minutes showed adhesion as good as ever; if heated for a longer period they blackened and became very brittle, but still showed good adhesion.

From these preliminary tests, it appears that the most important factors governing the occurrence of case-hardening in plywood or veneers are as follows:

(1) Inclination of grain to surface.
(2) Thickness of plywood (when dealing with veneers which have not been made up into plywood, thickness does not seem to matter).
(3) Nature of wood (heart or sap).

IV. Quantitative Experiments

These conclusions were confirmed by quantitative tests carried out on various samples of 3-ply. In order to investigate the effects of variations in the method of making up the 3-ply, arrangements were made to have several batches made up under controlled conditions.

The conditions under which this plywood was made were varied so as to try the effects of all possible combinations of the following variables:

Thickness	1 mm. or 2 mm.
Adhesive	Tego F/2 (135° C. and 355 lb./sq. in.) or Beetle Cement 'W' with hot hardener 12. (100° C. and 170 lb./sq. in.).
Position in press	Touching metal platens on one side, and next sheet on the other side. Touching the next sheet on both sides. Touching the wooden caul on one side, and the next sheet on the other side.
Rehumidification	Dipped in cold water after pressing, or not dipped.

The modified sandwich test was used, and six tests were made on each side of each board. For comparison, tests were also made on a sheet of 3-ply to specification 5.V.3, 0.8 mm. thick, which rough peeling tests had shown to be severely case-hardened.

All the above tests were carried out with a synthetic resin (urea-formaldehyde) glue—Beetle Cement 'A': results obtained in an earlier investigation at the R.A.E. show that the same effects occur with casein glues. In this investigation, specimens of tego-bonded birch plywood, 1 mm. thick, which had been pressed between metal platens, and had not been humidified after pressing, were tested by the old sandwich test, and it was found that the strength of the joints was low but was increased 50% if the surface of the wood was removed with sandpaper. A summary of all these results in the form of a block graph is given in Fig. 4.

V. Discussion of Test Data

The results confirm conclusions based on the results of the rough peeling tests; neither the use of wooden cauls, nor the practice of rehumidification after pressing, has any significant effect on the occurrence of case-hardening. It was not possible to establish any exact relation between the strength of the joint and the inclination of the grain to the surface because the latter could not easily be

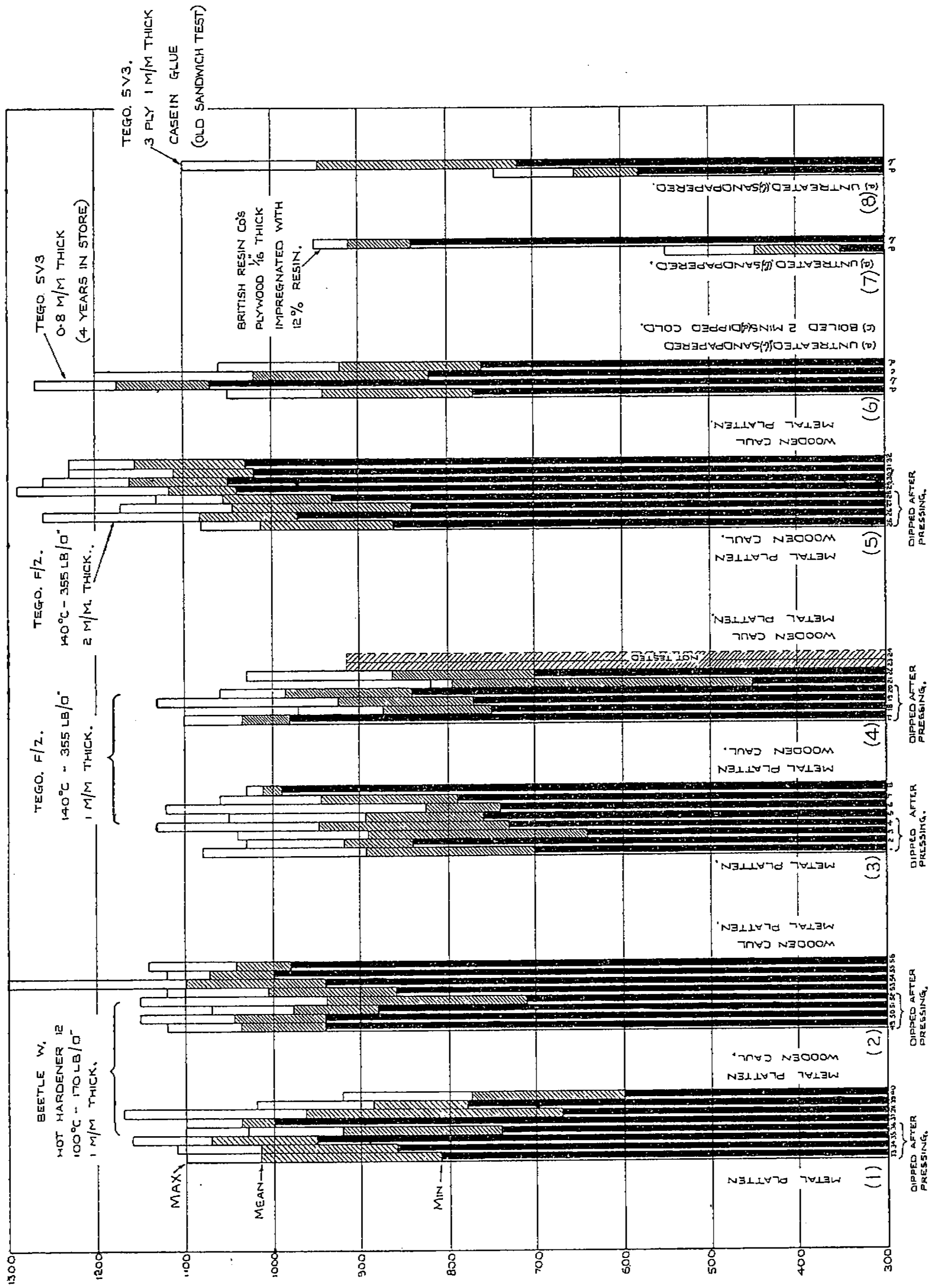


Fig. 4. STRENGTH OF PLYWOOD JOINTS
(For explanation see Appendix)

measured, but from examination of the broken surfaces, it was evident that very short grain always yielded a weak joint. The thick (2 mm.) boards all yielded much stronger joints than the thin (1 mm.) boards. If it is assumed that the effects of case-hardening are completely removed by sandpapering, then most of the 2 mm. boards are not case-hardened at all, as without sandpapering they yield joints nearly as strong as those obtained from the 0.8 mm. board after sandpapering. It is interesting to note that in the 2 mm. plywood, adhesion to the surface that has been rehumidified is worse than adhesion to the untreated surface.

VI. Factors Affecting Adhesion

As these conclusions do not agree with the hypothesis that case-hardening is due to dehydration of the cellulose in the wood, a re-examination of the evidence on which this theory is based was made.

Evidence for the irreversible dehydration of cellulose with the formation of covalent ether linkages between neighbouring chains is doubtful. It seems likely that there will be some change in the side chain spacing with changes in the water content similar to that observed in proteins, but an effect of this kind would probably be reversible. Kohman (1939)[2] could not find any evidence for the formation of ether cross-linkages in thoroughly dried paper from a study of its electrical properties. Stamm and Hansen (1937)[3] found that by heating wood it was possible to reduce the amount by which it swelled when immersed in water. It seems probable, however, that this result is due to condensation of the lignin component, and not, as the authors suggest, to the formation of ether linkages between cellulose chains. No change was observed when the specimens were heated in an atmosphere saturated with water vapour; this again is quite consistent with the idea that the effect is due to condensation of the lignin.

The only direct evidence in favour of de Bruyne's hypothesis is derived from a study of the angle of contact with water made by normal and by case-hardened plywood. It is claimed that the angle of contact is very much increased in case-hardened plywood, as might be expected if irreversible dehydration of the cellulose occurred. The method used to demonstrate this change in the angle of contact is a technique devised by Kohman (1939)[2] which has been described already (see Fig. 1). It is considered, however, that the results of this test will not bear the interpretation given to them, for the following reasons.

In the interpretation of the results proposed by de Bruyne, no account is taken of the microscopical structure of the wood, which is treated in fact as if it were a homogeneous solid with a plane surface. If the wood is treated as a system of intercommunicating capillary tubes of varying internal diameter, a completely different explanation of the results of the experiment is possible. When such a system is totally immersed in a fluid which wets the walls of the capillaries, the fluid penetrates some of the tubes, and drives bubbles of air out of others. The air bubbles have a tendency to stick in the mouths of the tubes: in order for a bubble to be released, work has to be done against surface tension at the air/liquid interface in order to increase the surface area of the bubble. The amount of work which has to be done depends on the diameter of the tube and the surface tension of the liquid. The energy to do this work has to be supplied by the forces which induce penetration of the fluid into the capillaries; the magnitude of these forces depends on the curvature of the meniscus in the capillary, which, in turn, depends on the diameter of the capillary and on the angle of contact which the fluid makes with the capillary wall (see Fig. 5).

The angles of contact of benzene and of water with the wood surface are probably both less than a right-angle. In sufficiently fine capillaries, therefore, the curvature of the meniscus of either fluid will approximate to a hemisphere, so that the forces tending to push a bubble off are much the same whether the wood is immersed in benzene or in water. The resistance to the release of the bubble, however, is much less in benzene than in water, because the surface tension of benzene is lower. In benzene, therefore, air will easily escape from the capillary spaces, and the liquid will penetrate the wood rapidly; in water, air will not escape so easily, and entrapped air will prevent the entry of liquid.

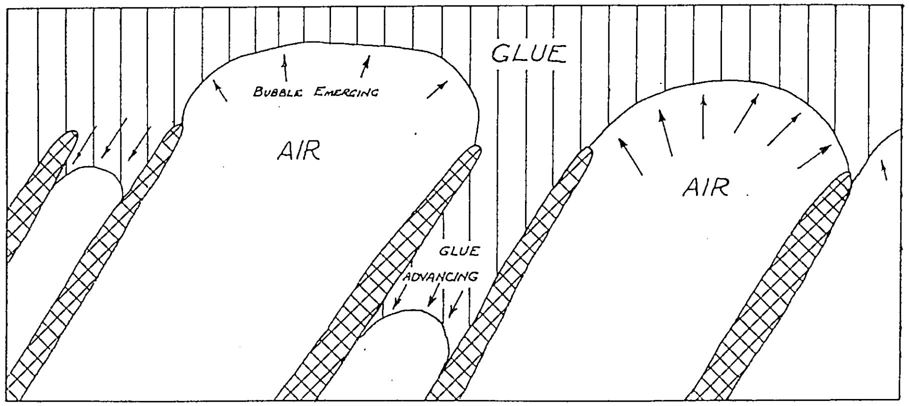


FIG. 5. DIAGRAMMATIC REPRESENTATION OF THE SURFACE OF WOOD AS SEEN UNDER THE MICROSCOPE

In the light of these considerations, the sequence of events in de Bruyne's experiments may be interpreted as follows: The wood is first dipped in water, which does not succeed in displacing air from the capillary spaces, and is then passed through a layer of benzene, or other non-polar solvent, into the layer of water below. The benzene displaces the air and fills the capillary spaces, so that a layer of it is carried down into the water, and the meniscus bends up into the benzene. The conditions governing the displacement of the benzene by water are similar to those governing the displacement of air by water.

This interpretation is supported by the fact that when a strip of plywood is immersed in water, the entrapped air can be seen as a silvery layer on the surface; when the same strip is immersed in benzene, the air is displaced and a cloud of small bubbles rises to the surface. If instead of merely immersing the sample in water before the test, it is held under water and well rubbed to ensure that all the air is displaced from the capillary spaces, the above conditions do not apply, and the meniscus bends downwards into the water. The experiment can thus be arranged so as to yield a positive or negative result at will. These results can be very easily demonstrated on a strip of baize or flannel glued to a piece of wood.

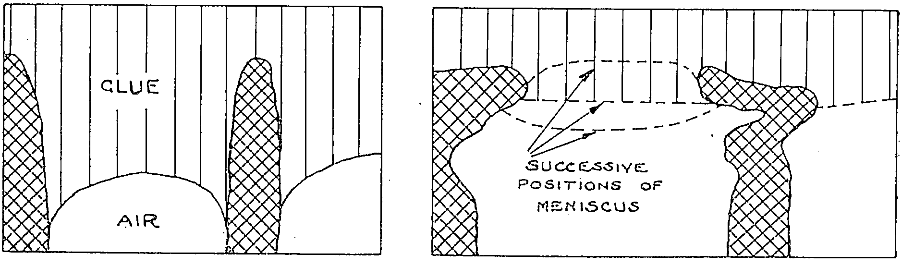


FIG. 6. DIAGRAMMATIC REPRESENTATION OF THE SURFACE OF WOOD AS SEEN UNDER THE MICROSCOPE

We may now consider the conditions affecting the penetration by adhesives of the capillary spaces of wood. Since glue is applied to one side of the wood only, it may be assumed that the air in the capillaries is free to escape; back pressure exerted by imprisoned air may then be ignored, and only capillary forces need be considered. If the internal diameter of the tubes remains constant right up to the open end, glue will penetrate the capillaries in the usual way (Fig. 5). If the cut ends of the tubes are compressed, however, so that they become burred over, the internal diameter near the ends is reduced and conditions for penetration by the glue become much less favourable. Suppose that the glue makes an angle of contact with the wood which is less than a right angle, but still not negligible; then if the angle which the burr makes with the horizontal is less than the angle of contact of the glue with the capillary wall, the meniscus in the convergent part of the tube will be convex downwards, and the glue will not penetrate the tube (Fig. 6), but will tend to stick in the narrowest part.

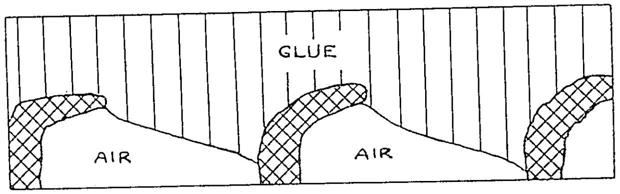
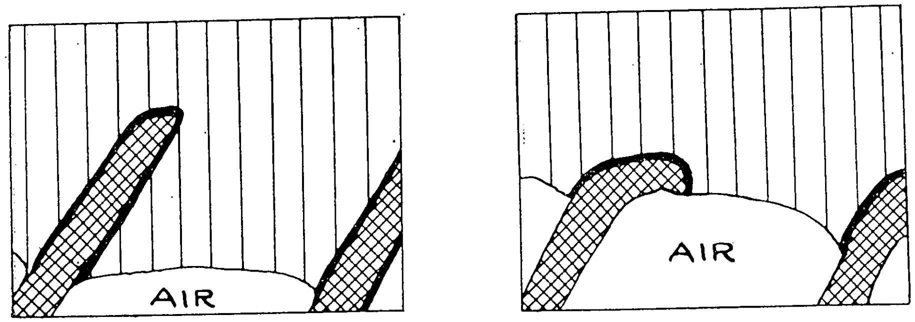


FIG. 7. DIAGRAMMATIC REPRESENTATION OF THE SURFACE OF WOOD AS SEEN UNDER THE MICROSCOPE

It is not necessary that both walls of the tube should be bent inwards; the same effect will be produced if they are all bent the same way (see Fig. 7).

Some burring-over effect of this kind may easily occur if the surface of the wood is compressed, particularly if pressure is exerted by a hot plate, which will soften the wood where it touches it. The walls of the tubes may also be bent over by the action of a blunt plane; this offers a probable explanation for the low strength of joints made to wood whose surface has been burnished.

The theory may be summarized diagrammatically by drawing a section of the wood in which the area in contact with glue is marked. It will be seen from this that the contact area is very greatly decreased if penetration of the capillaries is prevented (see Fig. 8).



Heavy line marks area over which glue makes effective contact with wood.

FIG. 8. DIAGRAMMATIC REPRESENTATION OF THE SURFACE OF WOOD AS SEEN UNDER THE MICROSCOPE

If no penetration occurs, there cannot be any mechanical interlocking of the glue and the wood, and the strength of the joint must depend entirely on the specific adhesion.

This mechanical theory of the nature of case-hardening explains satisfactorily the great importance of the inclination of the grain to the surface. From a consideration of the geometry of the system, it appears that the greatest reduction in the effective glued area will take place when the capillaries lie in a direction normal to the surface, i.e. with end grain. The reduction will be least when the capillaries lie in the plane of the glued surface; the cut surface will then consist of a series of troughs formed by cutting across cylindrical tubes at various levels. When the surface is crushed, troughs whose cross section is a segment of a circle less than a semi-circle will open out, and the rest will close in. On the whole, the decrease in effective glued area in the troughs whose edges bend inwards will be compensated for by an increase in the effective glued area due to the opening out of the other troughs, so that the total decrease in effective glued area will not be very large.

The mechanical theory of case-hardening will not explain why thin plywood should be worse than thick. This difference is probably due to accumulation of volatile and soluble constituents of the resin at the surface of the wood. de Bruyne has argued that case-hardening cannot be due to penetration of the wood by resin, because if the surface is rubbed down nearly to the glue line, adhesion is improved, although it might be expected that the veneer would be more thoroughly impregnated with resin near the glue line than at the surface. This argument does not take account of the soluble constituents of the resin. During the pressing of the veneers, water passes from the glue line to the surface, where it evaporates; this water carries with it soluble constituents of the resin, which are deposited in the surface layers of the wood, and there polymerise. The presence of a fully-cured resin impregnating the cell wall is likely to make the effects of the case-hardening more apparent, because the angle of contact which the liquid glue makes with the cell wall will be increased. The surface of thin sheets of tego-bonded plywood is often coloured pink or brown by resin; if the surface is removed by rubbing with sandpaper, the wood appears paler.

The effects of resin penetration were shown in an exaggerated degree by some special plywood which had been lightly impregnated with resin with the object of making it more waterproof; the veneers were impregnated with a water-soluble phenol-formaldehyde resin, so that the finished product contained about 12% of resin. This plywood showed extreme case-hardening; using the revised sandwich test with Beetle Cement 'A', the lowest of four values was 350 lb. (mean 447 lb.), and using casein cement the lowest value of five was 410 lb. (mean 552 lb.). When the surface layers were removed by rubbing with sandpaper, it gave values not far below those given by normal plywood (minimum of four 840 lb.; mean 910 lb.). (See Fig. 4.)

VII. Remedies for Case-Hardening

(a) Sandpapering

The effects of removing the surface layers of the wood by rubbing with sandpaper, or by cutting them off with a sharp plane, have already been mentioned. This treatment nearly always seems to effect a complete cure, both in plywood and in separate veneers. In one batch of $\frac{1}{16}$" birch veneers in which the grain was at an angle of about 60° to the surface, it was found, however, that rubbing away the surface of the wood with sandpaper did not very much improve the adhesion of Beetle Cement 'A'. The most probable reason for this failure is that when they are steeply inclined to the surface, the capillary vessels of the wood are so liable to "burring-over" at the end that it is impossible to cut them off clean by any method.

(b) Rubbing in the Glue

If the mechanical explanation of case-hardening is correct, the adhesion of glues to case-hardened plywood ought to be improved by rubbing the glue into the wood; the high local pressures caused by rubbing should force the glue past the narrow necks of the capillaries, after which it will penetrate the wood quite normally.

The effect of rubbing in the glue was tried out on some 5-ply birch 4 mm. thick (glued with tego-film), which preliminary tests had shown to be seriously case-hardened. Strips of the plywood were spread with glue with and without rubbing, and were then stuck on to a spruce board, and tested by the strip test at an angle of 30° to the horizontal (see Fig. 3). These tests yielded the following results:

Adhesive	*Treatment*	*Failing load (lb.)*	*Type of failure*
Beetle Cement 'A' ready mixed with hardener V.15.	Glue rubbed in with blunt spruce stick	36 42 48 50	In plywood.
		44	In spruce.
	Mean	44	
	Glue not rubbed in	20 23 24 25	Between glue layer and plywood.
		36 36	As above, except for small strip along edge which has failed in spruce.
	Mean	27	
Casein	Glue rubbed in	53 53 64	Failed in plywood.
	Mean	56	
Casein	Glue not rubbed in	37 41 44	Mostly between glue and plywood, leaving some wood fibres in glue.
	Mean	40	

Similar experiments were carried out on samples of 5.V.3 3-ply, 0.8 mm. thick (the same sheet as was tested by the modified sandwich test), using casein glue. These were tested at a steeper angle (60° to horizontal) because at smaller angles the strips failed in bending when adhesion was good. These tests yielded results as follows:

GLUE RUBBED IN

	Load in lb.	*Type of failure*
	27	Glue.
	31	Spruce.
	37	Glue and fibre.
	38 (3)	Plywood and partly in glue.
	41 45 49	Plywood.
Mean	38	

GLUE NOT RUBBED IN

	11 (4) 14 15 17 19	Between glue and plywood.
	31	Part glue, part plywood.
Mean	15	

These results show that to rub the glue into the plywood is an effective remedy for case-hardening. A disadvantage of this process is that casein glue is liable to become very frothy during the rubbing process: this does not apply to synthetic resin glue, which does not froth easily.

(c) Damping the Wood

It has been shown already that dipping the plywood after pressing does not have any significant effect on the occurrence of case-hardening. The effect of rubbing the surface with a wet sponge was also investigated on a sample of the 0.8 mm. 3-ply used for some of the other tests; no improvement in joint strength was obtained. Boiling the strips in water for two minutes did have some effect, but this is hardly a practicable remedy (see Fig. 4).

(d) Pressure

A series of small samples of the case-hardened 0.8 mm. 3-ply was glued up with Beetle Cement 'A' under a clamping pressure of about 200 lb./sq. in. and tested by the rough peeling test. The adhesion was uniformly bad and the broken surfaces were typical of case-hardened plywood.

(e) Effects of Long Storage

It has been suggested that the effects of case-hardening wear off with time. This is not so; some of the worst plywood tested had been in store for four years.

VIII. Appendix

Description of Fig. 4

Each column represents the results of six tests made on one surface of a sheet of plywood. The height of the black part of each column represents the lowest value obtained; that of the cross hatched part the mean, and the unshaded part the maximum. The first five groups show the results of tests on plywood made up under controlled conditions; the results are arranged in the order in which the sheets lay in the press. For example, in group 5, the first column represents the upper surface of the top sheet of a batch of four sheets that were pressed together; this surface was next to the metal platen. The next column represents the lower surface of the same board, and the third column the upper surface of the second sheet.

The sixth group shows results obtained on a typical commercial sample of case-hardened plywood, and illustrates the effects of sandpapering.

The seventh group shows results obtained on plywood which had been impregnated with about 12% of a phenol-formaldehyde resin.

The eighth group shows results obtained using casein glue, and the original sandwich test, on a sample of case-hardened plywood (part of the experimental batch, pressed between metal platens and not rehumidified).

IX. Bibliography

[1] N. A. de Bruyne. *Flight*. 18 Dec., 1939.
[2] G. T. Kohman. Ind. Eng. Chem., 1939. *31*, 807.
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Report No. 3

Adhesion of Glues to Plywood (Part II)

(Based on R.A.E. Report MAT/N/2/2001, January, 1944)
by Dr. M. G. M. Pryor and Miss C. M. Gordon

U.D.C. No. 668.3 : 674-419

Abstract

The sequence of causes leading to a typical failure of "case-hardened" or "stripped" type may be summarised as follows:

1. The number of cells penetrated by glue is decreased because of crushing and blocking. This effect may be intensified by the results of impregnation of the ends of the cell walls with resin.
2. Crushing also has the effect of diminishing the surface accessible to the glue without penetrating the capillaries.
3. What surface is then available is of little value because it consists partly of debris and of bruised cell walls which have little strength.
4. The general decrease of surface area due to (1) and (2) makes it more difficult for water to escape from synthetic resin glues, and leads to emulsification and consequent failure of adhesion.

Plywood giving weak glued joints usually has in its construction veneers which give weak glued joints. Such veneers are made worse by being crushed in the press and also by being impregnated by resin ascending from the glue line. Good veneers usually give good plywood.

Adhesion can be improved by mechanical sandblasting of the plywood with air-borne or centrifugally projected abrasives.

Contents

CONTENTS—*continued*

Illustrations

I. Introduction

In Report No. 2, factors affecting the adhesion of glue to plywood were discussed, with particular reference to a characteristic type of failure which was known as the "case-hardened" type. The appearance of a typical failure of this kind is shown in Fig. 1; the plywood has peeled off the glue entirely, leaving exposed a clear layer of glue without any adherent wood fibres. The surface of the glue bears a fine cast of the outline of the wood.

The expression "case-hardened" is not very appropriate and suggests a false analogy with the case-hardening of metal, and it has therefore been abandoned entirely. The type of adhesion failure which in Report No. 2 was taken as characteristic of "case-hardened" plywood is now called the "stripped" type of failure; plywood which gives this type of failure is called "non-gluing plywood".

Stripped failures are common in service, and this defect is probably responsible for a large proportion of the failures of glued joints reported; the Appendix gives a list of accidents and defects in which stripped failures have been reported.

In Report No. 2 sanding of the plywood before gluing was recommended as a means of preventing stripped failures, and sanding of all plywood was later made compulsory for aircraft parts. It was found, however, that this requirement was difficult to enforce and caused delay in production, and to avoid these objections it was decided to sand all plywood before it was issued to aircraft manufacturers. To do this it is essential to adopt some method of machine sanding; before ordering the necessary machinery it was felt that the investigations described in the previous report should be checked and extended.

II. Tests for Gluing Properties of Plywood

It has been impossible to use the same test joint for all the experiments but a numbered list of the types used is given, together with sketches of those which have not been described in previous reports. The tests will be referred to by these numbers:

(1) A 1 in. square of plywood is sandwiched between walnut slips as used in the B.S. 3.V.2 test. Two surfaces are tested simultaneously. The large ratio of the edges of the joint to its internal area provides very artificial conditions. This is the "old sandwich test" of Report No. 2.

(2) A modification of No. 1 in which one surface only is tested and edge effects reduced; this is described and illustrated in Report No. 2 as the "modified sandwich test" (Fig. 2). Satisfactory joints fail at a load of about 1,100-1,200 lb.; joints which give stripped failures at about 600-300 lb.

(3) A modification of No. 2 in which a 1 in. lap-joint is made between two walnut strips to B.S. 3.V.2, both of which are faced with plywood.

(4) A 2 in. square of plywood is sandwiched between beech veneer slips as used in B.S. 4.V.2. The glued area of the plywood is reduced to 1 sq. in. by covering all but the terminal inch of the beech with Cellophane. Two surfaces are tested simultaneously. Satisfactory joints fail at a load of about 700 lb., non-gluing joints at 550-300 lb. (See Fig. 3.)

(5) A $\frac{1}{2}$ in. overlap joint between unbacked strips of plywood 1 in. × $4\frac{1}{2}$ in.: the breaking load varies with the stiffness of the ply and is therefore different for different thicknesses.

(6) Pull-off tests made by gluing strips of ply 1 in. wide on to spruce to give an area of adhesion of 1 sq. in. and pulling them off by attaching a bucket to the free end and loading it with lead shot. The length of strip was arbitrarily increased with the thickness of the ply. The failing load is taken as the weight of the bucket and shot when the joint breaks (see Fig. 4).

(7) A qualitative test by gluing a patch of fabric on to the wood and stripping it off after the glue has set but before it loses its plasticity. With plywood which glues well, a layer of glue is left on the surface; with non-gluing plywood, the glue strips clean off (see Fig. 5).

Each of these tests has its drawback; No. 6 imitates the conditions of a glued joint between the skin and spars better than the others, but the figures obtained are only of relative value because they are largely dependent upon the stiffness of the ply; the same objection applies to No. 5. No. 3 and No. 4 have now been used extensively, but they are not as sensitive as tests in which there is a large tensile component of the load acting normal to the surface.

An inspectional test for the gluing properties of plywood which does not involve making and breaking a joint, has so far not been discovered by the authors.

III. Incidence of Defective Gluing with Different Kinds of Wood

Stripped failures occur most commonly when two pieces of ply are glued face to face, as in the joint between the skin and the capping strip on the ribs or spar flanges of the wings of some aircraft. It also shows in ply-spruce joints, particularly where the load tends to push the ply off, rather than to pull it in shear. In such cases the glue stays firmly attached to the spruce, but comes clean away from the plywood.

The frequency of occurrence of non-gluing properties in birch plywood is shown by the following series of tests (test No. 3). Out of 138 tests on 21 different boards of 0.8 mm. birch plywood to B.S. V.3 the mean failing load was 838 lb. and 30% of the results fell below $\frac{2}{3}$ of the mean value (standard deviation 20% of mean). 126 tests on end-matched specimens from the same boards which had had the non-gluing surface removed by sanding gave a mean failing load of 1,064 lb. and only 0.1% of the results fell below $\frac{2}{3}$ of the mean failing load for the untreated specimens (standard deviation 15.8% of the mean of the sanded specimens).

The frequency of occurrence of stripped failures in joints between two plywood surfaces (test No. 5) does not decrease with the increasing thickness of the ply. The results plotted in Fig. 6 show that although the breaking load rises with increase of thickness (possibly with the square root of thickness) the difference between the sanded and unsanded wood remains approximately constant. In plywood members stripped failures have occurred in these tests more frequently with the thinner grades; this is probably because there is more peeling action in the breaking of the joints than there is with stiff, thick plywood. As will be seen from the histogram (Fig. 7) the bulk of the ply used in aircraft is of the thinner grades.

Stripped failures are not confined to birch plywood; serious trouble in service has been experienced from $\frac{1}{16}$" guarea plywood, and in laboratory tests stripped failures have been obtained from plywood made of beech, spruce and gaboon. Table 1 gives results obtained on guarea plywood with a birch core. The tests were made on both sides of six different boards (test No. 2).

FIG. 1. TYPICAL STRIPPED FAILURE
Casein glue to B.S. 4.V.2. Joint between plywood skin and spruce spar of tailplane.
Magnification x 1.

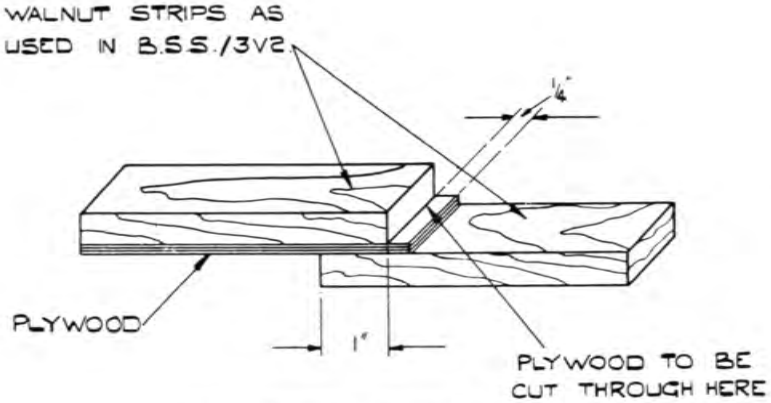
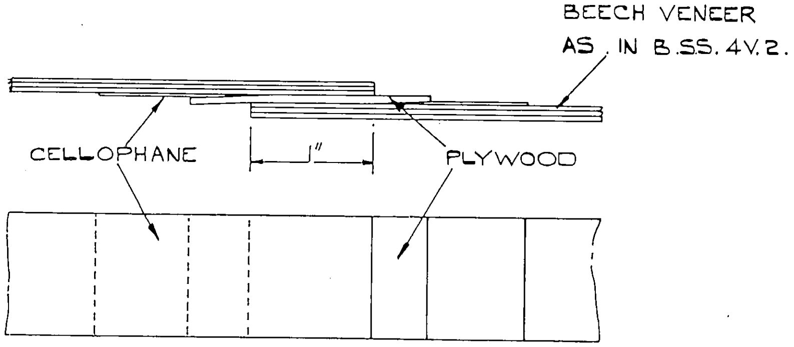
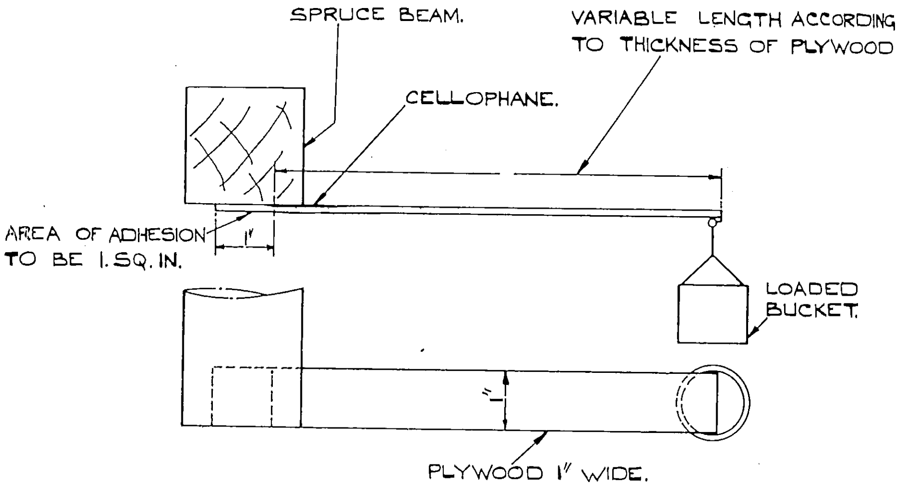


FIG. 2. MODIFIED SANDWICH TEST



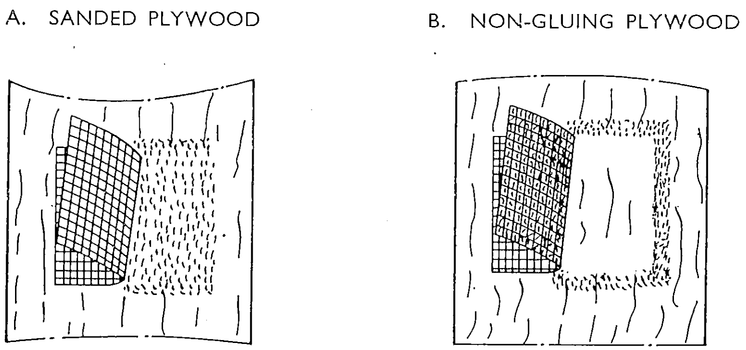
Test Type No. 4

FIG. 3. ADHESION TESTS ON PLYWOOD



Test Type No. 5

FIG. 4. ADHESION TESTS ON PLYWOOD



A. SANDED PLYWOOD

B. NON-GLUING PLYWOOD

Test Type No. 7

FIG. 5. ADHESION TESTS ON PLYWOOD

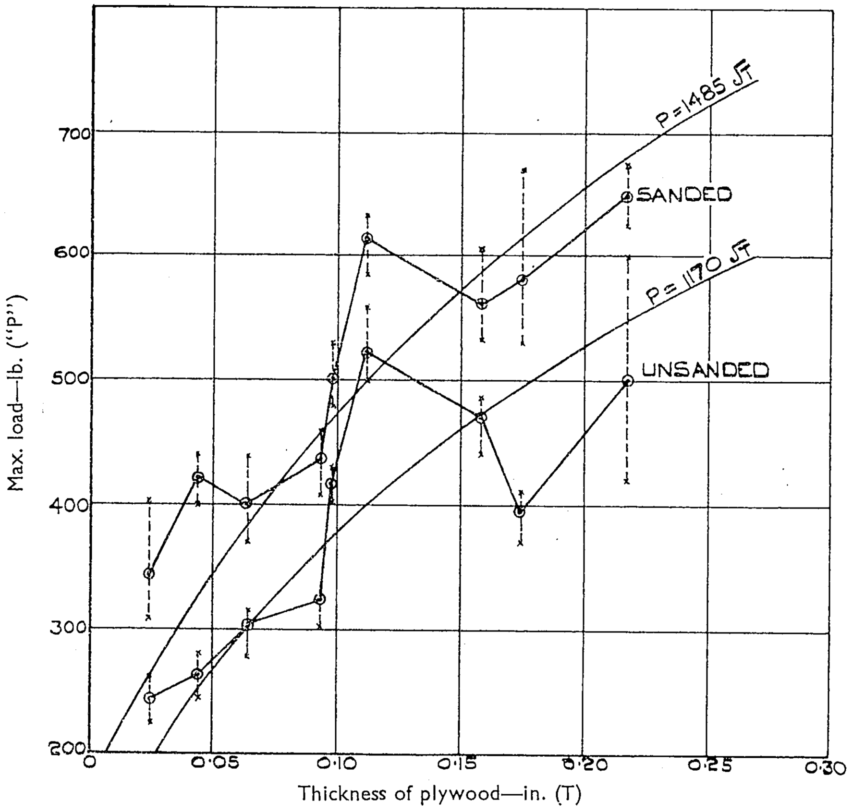


FIG. 6. STRENGTH OF LAP-JOINTS BETWEEN DIFFERENT THICKNESSES OF PLYWOOD

(O = Mean value, X = Min. or Max. of Batch of 12. Test Type No. 5)

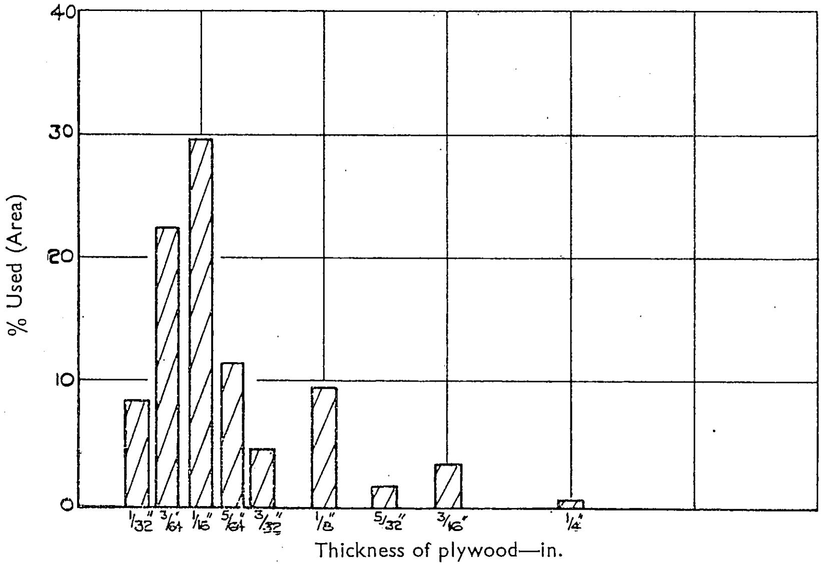


FIG. 7. AMOUNT OF PLYWOOD OF DIFFERENT THICKNESSES USED IN AIRCRAFT CONSTRUCTION

TABLE 1

Unsanded *Mean failing load* (*36 tests*)	*Sanded* (*by hand*) *Mean failing load* (*36 tests*)
730 lb.	828 lb.

Stripped failures may occur with veneers as well as with finished plywood. Non-gluing veneers, which will not glue even under heat and pressure, may give rise to defects in "compreg" wood boards of the type manufactured with paper film glue.

Stripped failures very like those given by plywood are the rule with vulcanised fibre, which cannot be glued effectively unless it is sanded.

IV. Incidence of Defective Gluing with Different Kinds of Glue

The connection between the frequency of stripped failures and the type of glue used was investigated thoroughly only for an unfilled urea-formaldehyde resin glue (to D.T.D. 335A) and a casein glue. The results in Table 2 look at first sight as if the casein were slightly less prone to stripped failures than the urea glue, but on statistical analysis the difference proves to be not significant ($t = 0.71$; $n = 12 + 12$).

TABLE 2. COMPARISON OF UNFILLED SYNTHETIC RESIN GLUE TO D.T.D. 335 AND CASEIN GLUE TO B.S. V.2

	Synthetic resin			Casein		
	Min.	Mean	Max.	Min.	Mean	Max.
Series A						
Unsanded	540	594	670	490	585	720
Sanded	995	1039	1100	790	919	1000
Difference		445			334	
Series B						
Unsanded	375	714	920	550	656	780
Sanded	920	1049	1100	830	884	950
Difference		335			228	

Results represent average failing loads in lb. of batches of six tests on 0.8 mm. birch ply sandwiched between walnut (Test Type No. 1).

Some further results upon the comparative sensitivity of pressed veneers to stripped failures, using four different glues, will be found in Section V (a) 3. There are not enough results to apply statistical methods, but here again the difference is probably not significant. The occurrence of stripped failures is not confined to any one type of glue.

V. Factors Contributing to Bad Adhesion

(a) **Damage to the Surface of the Wood**

1. MECHANICAL DAMAGE

When the surfaces of plywood or veneers are examined either by the naked eye or microscopically it is impossible to see any difference between those which glue well and those which yield stripped failures.

Sections normal to the surface were cut in a sledge microtome, but it was found that the all-important outer layer of cells was usually lost. To avoid this, the surface was guarded with a film of collodion, hide glue, or cold-setting phenol-formaldehyde resin; if this film is intact on the section it is certain that one is really looking at the original outer cells and not at a freshly-torn edge. The difficulty is that in sections of non-gluing wood, the adhesion is so poor that the film often becomes detached during the preparation of the slide.

Decrease in surface area

Plywood which glues well (whether initially or as the result of sanding) has an edge whose contour is sharp, clear-cut and free from fragments or compacted cells (see Figs. 8 and 10). The outline of similar sections of non-gluing ply is often fuzzy owing to frayed ends, bent cell lips, and general debris (Figs. 9 and 11), but the adhesion can be very poor when the section of the surface looks as clean and firm as the sanded wood. The occurrence of an undamaged surface in some sections of non-gluing ply is probably due to the fact that one section is an extremely small sample of the surface (about 0.002 sq. cm.), while a single test joint represents the effective adhesion for 6.5 sq. cm.; variation is considerable even as between different samples of 6.5 sq. cm., so that the occurrence of an undamaged section in a sample which in general will not glue, is not at all improbable.

In non-gluing plywood with the bruised type of surface, the area of contact available for the glue appears to be less than the area available when the surface is undamaged. To check this, tracings were made from a projected image of the surface of sections of many samples of sanded and unsanded plywood, and the ratio between the straight length of the edge and the length of the contour was obtained.

TABLE 3. RATIO OF CONTOUR TO STRAIGHT LENGTH OF EDGE

Sanded plywood, adhesion good	*Unsanded plywood of all types, with bad adhesion*		
2.2	1.07	1.7	2.15
2.25	1.6	1.75	1.45
2.0	1.1	2.0	
2.5	1.3	2.05	
2.6	1.2	1.36	
Average 2.31	Average 1.56		

If we assume that the surface of straight-grained wood has an increase in adhesion area in one direction only, like a sheet of corrugated iron, then the area of the sanded wood is 1.5 times greater than the unsanded. Assuming that joint strength is simply proportional to the area of contact between glue and wood, and if a joint to unsanded plywood fails at 700 lb., then the same wood sanded should give a joint strength of 1,050 lb. In practice, well-sanded joints usually fail in the wood at about 1,200 lb. so that the real increase in glue strength is more than one and a half times.

Blocking of cell openings

In Report No. 2 it was suggested that if the edges of the cells were bent over glue would be unable to enter, because the curvature of the advancing meniscus would be reversed.

To check this idea, model capillaries with expanded or inbent lips were made out of glass; these were submerged in a mixture of a phenol-formaldehyde resin glue and hardener and the penetration of the glue was watched through a low-power microscope. It was found that penetration was only prevented if the lips were bent in until they were nearly parallel with the sides of the tube. If we take the glass capillaries as representing the conditions in the wood, this means that in practice burring-over of the cell wall is probably not an important factor in preventing the penetration of glue into the wood, because in very few capillaries are the ends likely to be bent through more than a right angle.

It is difficult to observe in birch the condition of the ends of wood vessels which have been cut or broken transversely to their length, because it is hard to cut longitudinal sections less than one cell thick, and the sections when prepared are often distorted. Sections were therefore made of spruce, in which synthetic resin glue had been allowed to penetrate from an end-grain surface. If the penetration of glue into end grain exposed by a saw cut is compared with that into the clean surface obtained by fracture, it appears that penetration is only prevented if crushing is sufficient to close the end of the capillary completely. If these conclusions apply to birch, as they probably do, it appears that the previous theory was unnecessarily elaborate, and that it is simply closing of the ends of the capillaries rather than burring-over of their lips which prevents penetration.

Bruising of ends of cells

Another mechanical factor which is of considerable importance is that a surface of damaged cells and loose debris gives a weak anchorage for the glue. Small "whiskers" of wood left on the glue of a stripped failure are a familiar feature, and in a section of such a failure in its earliest stage one can see how the glue has stuck to the surface of the wood, but this surface being rotten has come away with the glue (Fig. 12). The same thing can be seen when a dried layer of collodion (cellulose nitrate solution) is stripped off non-gluing veneer (Fig. 13); the weak pieces are removed and the sound wood with its open cells left behind. Since this surface resembles a sanded one (Fig. 8) it ought to glue well, and pull-off tests (No. 6) were done on a sample of non-gluing birch veneer 1 mm. thick, both treated with collodion, untreated, and hand sanded.

TABLE 4. ADHESION OF 1 MM. BIRCH VENEER, FILLED UF GLUE TO D.T.D. 484 (TEST TYPE NO. 6)

	Untreated	*Sanded*	*Collodion peeled off*
	2.80 –	4.05 +	3.35 +
	3.90 +	3.30 +	4.15 +
	2.10 –	2.90 +	4.20 +
	1.52 –	3.50 +	5.80 +
Average	2.58	3.44	4.38

(+ = wood failure ; – = stripped failure)

Thus collodion is as effective in improving adhesion as sanding. One would expect that this same batch of veneer could also be cured by peeling off glue, which should take the bruised wood with it in the same way as collodion does. To try this, test pieces which had failed between the glue and the wood without damaging the wood were reglued and pulled again.

TABLE 5. TEST TYPE NO. 6

	Original failing load	*Reglued*
Synthetic resin glue to D.T.D. 484	Average 2.55 lb.	Average 2.36 lb.
Casein glue	4.82 lb.	3.80 lb.

The failures were of the "stripped" type throughout, and there was a slight deterioration in the joint-strength upon the second gluing. This result is unex-

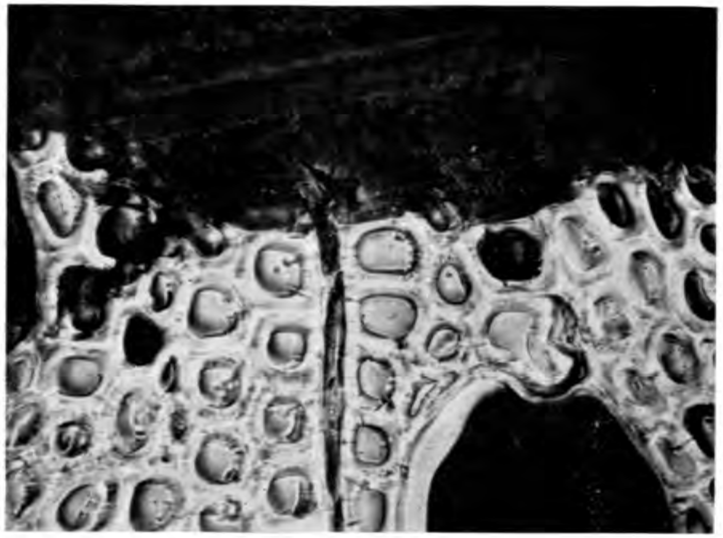


FIG. 8. TRANSVERSE SECTION OF THE SURFACE OF SANDED PLYWOOD GLUED WITH PF GLUE TO D.T.D. 484 AND THEN STAINED
Magnification x 375.

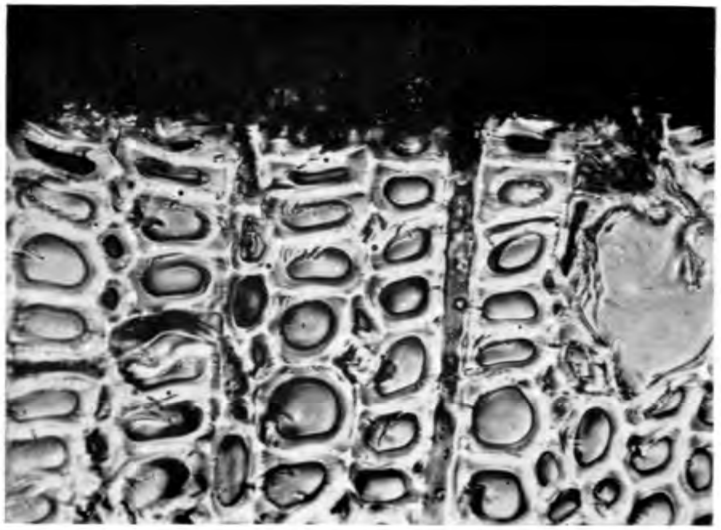


FIG. 9. TRANSVERSE SECTION OF THE SURFACE OF UNSANDED PLYWOOD GLUED WITH PF GLUE TO D.T.D. 484 AND THEN STAINED
Magnification x 375.

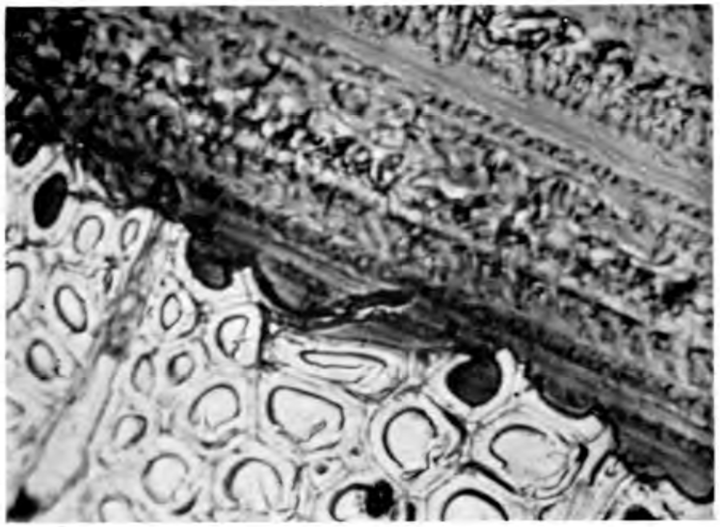


FIG. 10. TRANSVERSE SECTION OF THE SURFACE OF SANDED PLYWOOD GLUED WITH PF GLUE TO D.T.D. 484 AND THEN STAINED
Magnification x 480.

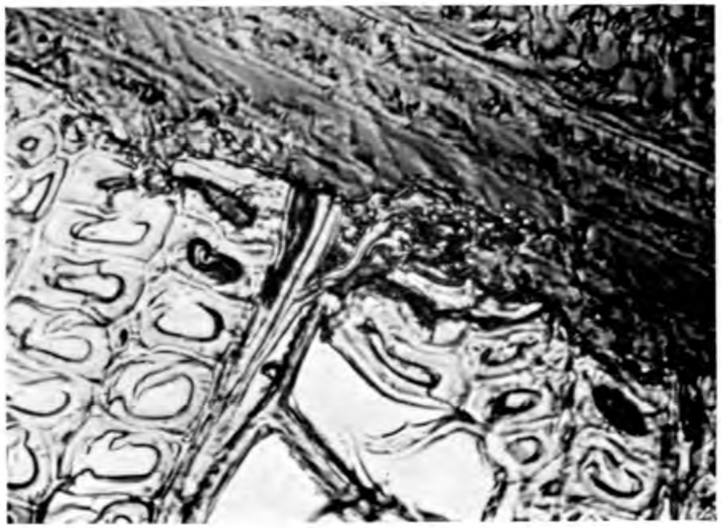


FIG. 11. TRANSVERSE SECTION OF THE SURFACE OF UNSANDED PLYWOOD GLUED WITH PF GLUE TO D.T.D. 484 AND THEN STAINED
Magnification x 480.

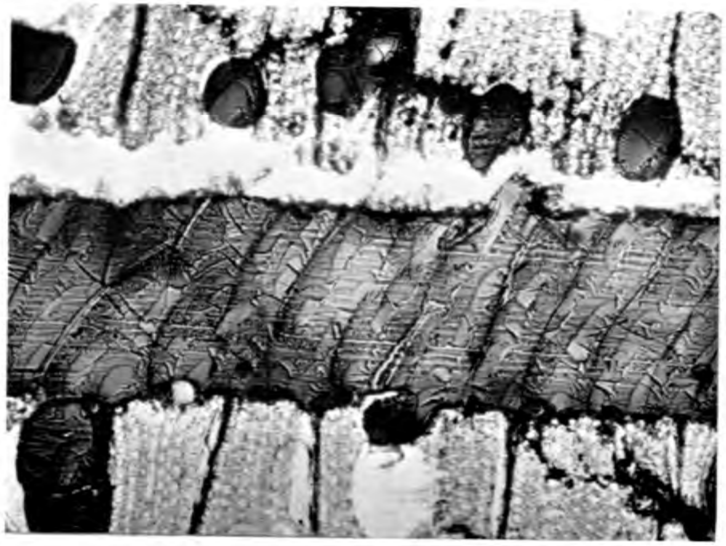


FIG. 12. TRANSVERSE SECTION OF JOINT BETWEEN NON-GLUING VENEER (UPPER) AND SANDED VENEER (LOWER). PF GLUE TO D.T.D. 484
Magnification x 80.

FIG. 13. COLLODION PARTLY STRIPPED OFF. NON-GLUING PLYWOOD
Magnification x 150.

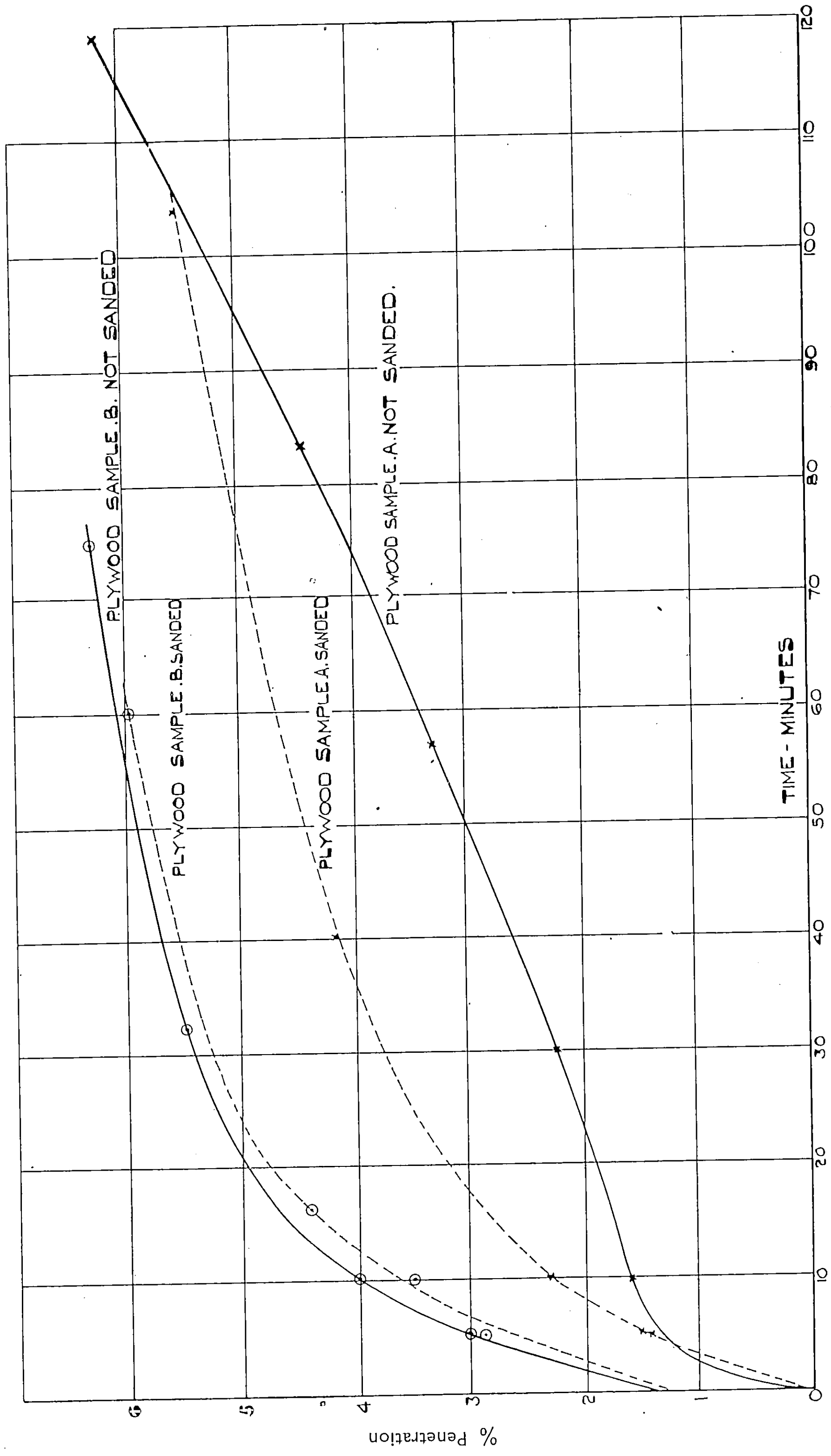


FIG. 14. PENETRATION OF GLYCERINE INTO PLYWOOD
Non-Gluing and Sanded Plywood.

pected, and it was thought that the solvent in the collodion might have something to do with it. Test pieces of the same sheet of veneers were therefore subjected to an ether-alcohol extraction in a soxhlet for 2 hours, and when dry were tested as before; the results are given in Table 6.

TABLE 6. 3 in. x 1 in. PULL-OFF TESTS NO. 6. SYNTHETIC RESIN GLUE WITH FILLER (D.T.D. 484)

Veneer untouched	*Extracted and dried*
4.0−	3.9−
3.3−	2.4−
5.6+1	5.8+

These results show that the good effects of the collodion treatment cannot be due to its solvent. A possible explanation of the failure of glues to act in the same way may be that they stick too well. One can see under the microscope that where the glue has made contact with sound wood it has snapped off, leaving fragments behind which block the capillaries. With collodion the adhesion is so very poor that no sound wood is uprooted or parts of the adhesive film broken off, and only bruised fragments of wood are taken away.

Summarising this section, we may say that the mechanical damage to the wood surface consists of:

(1) A flattening of the surface, which reduces the effective gluing area.

(2) Blockage of cell entrances by collapse of their walls and by fragments.

(3) Injuries at the base of the projecting cell walls.

These features are not found in ply which glues well; they are frequently, though not invariably, found in non-gluing ply.

2. CHEMICAL DAMAGE

The microscopic examination of non-gluing ply and veneers has shown so far that the morphological character of the surface may be slightly changed. It remains to examine the staining reactions of the surface cells for signs of chemical damage.

The wood gives normal staining reactions with the usual botanical stains such as malachite green, basic fuchsin, methylene blue and neutral red. There are special stains for the glue which have been developed by the Forest Products Research Laboratory* and others for detecting the effect of phenolic resins on fibres, worked out at R.A.E. Sections of unsanded, non-gluing, birch plywood (to B.S. V.3) can be stained to show the presence of polymerised phenol-formaldehyde in the glue film resin, using either neutral red chloride, Martius yellow, erythrosin or a bromine stain. In all cases the resin of the film glue with its enclosed paper fibres can be seen as a layer between the veneers with frequent pillars extending up into the medullary rays and also into the neighbouring wood cells. Even when the veneer is less than 0.3 mm. thick, the resin does not percolate more than one-quarter of the way across it, and does not appear on the surface of the wood, so that simple penetration of phenolic resin cannot be a general cause of non-gluing properties. There is, however, in plastic sheet a peculiar modification of the fibre by the resin which can be shown by its staining bright red with aqueous methyl red. If this test is applied to sections cut by slicing off the outer layer of plywood, the medullary rays, which are cut transversely and go straight down to the glue film are coloured scarlet, while the tracheides and normal wood cells which do not communicate directly with the resin, are very pale pink or even colourless.

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*Rendle, B. J. J. Soc. Chem. Ind., 62,1,11.1943.

This means that the cell walls which have been "kippered" by the ascending resin fumes are no longer behaving as ordinary lignocellulose. The same phenomenon in an exaggerated form occurs in ply made from deliberately damped (and therefore plasticised) glue film, where the whole surface of the plywood is rose coloured. In Report No. 2 the reasons for this effect being confined to the surface have been discussed. In veneers there is no surface reaction, although the rays and occasionally the middle lamellae of the cell walls are coloured pink, which is presumably due to their impregnation with natural resins having free acidic groups which react with the methyl red.

The effect upon adhesion of this modification of the fibre by the resin was tested experimentally by finding the angle of contact which glues made with fibres which had been in contact with resin. The microscopic method of Adams* was used, and as wood splinters were too short and rough, bast fibres of jute were substituted. The peculiar viscous properties of glue made the angle of contact difficult to determine, so that only approximate values could be obtained. (See Table 7.)

TABLE 7. CONTACT ANGLE OF GLUES TO JUTE FIBRES

Treatment of fibre	Phenol-formaldehyde resin + hardener	Urea-formaldehyde resin (unfilled) + hardener
100° C. 1½ hrs.	0-10° advancing	10°-30° advancing
100° C. 1½ hrs. + phenol	5-15° ,,	35°-50° ,,
,, + formalin	5-15° ,,	50° ,,
,, + PF resin	25-30° ,,	100°-120° ,,
,, + UF resin	5-20° ,,	85° ,,

The phenol-formaldehyde glue used contained a wetting agent, which is probably the cause of it being less sensitive to changes in the fibre than the urea glue. The only remarkable thing is that the urea-formaldehyde resin makes an angle of more than 90° to a PF resin-treated fibre, which means that if it were in such a capillary it would behave like mercury in a glass capillary, having a negative angle of contact and never ascending. In order to test the practical results of this, 4 mm. birch veneers were treated in the same way as the jute fibres, and their gluing assessed on pull-off tests (No. 6); results are given as percentages of the failing load of the untreated veneer, on an average of six tests (Table 8).

TABLE 8

Treatment of veneer	Phenol-formaldehyde resin to D.T.D. 484	Unfilled urea-formaldehyde resin to D.T.D. 335A
Nil	100	100.0
PF resin air dry	105	98.2
PF resin 160° C. 10 mins.	96	43.0
Same sanded	100	98.0

The only time when the strength of the joint is seriously affected is under conditions which might be expected to increase the angle of contact to more than 90°. Transverse sections of these resin-treated veneers showed that the condensed resin never forms a continuous surface layer, and although individual cells are filled with resin their outer walls are always colourless, but the same sections stained with methyl red showed that the walls of the outermost cells had been modified by the presence of the resin and give a typical red reaction. Therefore once again the effect of impregnation in reducing joint strength is not due to the presence of the free resin as such, but to the formation of a loose compound or very intimate mixture between resin and the substance of the cell wall. This finding confirms the conclusions reached in Report No. 2.

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*Adams, N. K. Contribution to "Symposium upon Wetting and Detergency." Harvey, London. 1937.

3. HOW THE DAMAGE IS DONE

It is very rare to have any difficulty in gluing natural timber, but peeled veneers sometimes give trouble, and plywood very often does. Therefore the plywood must acquire its non-gluing surface during some process of its manufacture, and by following the board backwards from its final, non-gluing state to the unpeeled timber, it ought to be possible to find out at what stage it acquires non-gluing properties.

Mechanical damage

Pressure

Where crushing of the cell walls is an important factor, one might expect some correlation between the behaviour of the plywood with glue and the pressure at which it was made. Plywood presses usually work at pressures between 170-260 lb./sq. in. In previous experiments (see Report No. 2) it was found that some veneers could be pressed hot up to 1 ton/sq. in. without affecting their gluing qualities, while others became non-gluing at less than 100 lb./sq. in. Since then, further quantitative tests have been made. The results in Table 9 were obtained with a urea-formaldehyde resin glue to D.T.D. 484 (wood-flour filled) and show that it is usually necessary to have a veneer with initially bad adhesion for the pressure to be able to make it worse. Given a good veneer to start with, it usually remains good at ordinary manufacturing pressures, even though pressed against metal, but a bad veneer responds to heat and pressure by becoming even worse.

TABLE 9. PRESSURE-VENEERS

Urea-formaldehyde resin (with filler) to D.T.D. 484. Average load (lb.)

Pressure applied to veneer		Sanded	Unsanded						Remarks
		0	0	250	500	600	1,000	1,200	
Veneer thickness 4 mm.		5.80 5.40	5.06 4.69	4.9	4.71		2.68	2.22	Test type No. 6 No. of tests 5
1 mm.	B	4.0	4.0			3.90			Test type No. 6 No. of tests 6
	A_1	4.7	3.1			2.25			Test type No. 6 No. of tests 6
	A_2	652	317	349	326		398	342	Test type No. 4 No. of tests 5
0.3 mm.		742	735	732	639		737	760	Test type No. 4 No. of tests 4

All results are means of 6 tests. Veneers all pressed at 160° C. against degreased copper platens.

Position in press

In Report No. 2 it was concluded that the position of the board in the press does not have much effect on its gluing properties. Test figures from several sources have been collected in Table 10. The three groups are not strictly comparable; the only valid comparisons are P with P and B with B. Within the batch P there is no significant difference between the behaviour of sheets pressed against each other and that of sheets pressed against metal platens, but the number of tests in the two classes is very different (60 : 10). There is a significant difference (t = 3.44, n = 30 + 40) between the B batches, which is in favour of the central position.

TABLE 10. EFFECT OF POSITION IN PRESS ON GLUING PROPERTIES

Position	Test used	No. of tests	Mean failing load (lb.)	Glue used for test joint	Batch No.
Against next sheet	No. 2	61	893	Filled UF to D.T.D. 484	P
Against metal platen	No. 2	10	939	,, ,, ,,	P
Against next sheet	No. 1	30	644	Unfilled UF to D.T.D. 335	B
Against metal platen	No. 1	40	588	,, ,, ,,	B

To conclude, the position in the press may have some effect on the properties of boards, but the effect is slight and probably of no practical importance.

Chemical damage

Effect of bonding glue

The bonding glue used between the veneers has been shown to affect the adhesion of glues to the plywood (V (a) 2). In Table 11 are given the strengths of plywood joints tested with a urea-formaldehyde resin (filled) to D.T.D. 484 when the ply has been made up under ordinary pressing conditions (100-140° C. and 170-360 lb./sq. in.) using different bonding glues. There is a significant difference (t = 7.18) between plywood made with a hot-setting urea-formaldehyde resin and with a phenol-formaldehyde paper film. Statistical analysis of these results shows that in this batch of tests the chance of a test piece failing at a load of less than 700 lb. is ⅓ for the PF film bonded ply, and 1/160 for the ply made with the UF resin.

Susceptibility of veneers

We have seen that the initial gluing qualities of a veneer have some effect upon its susceptibility to pressure, and from this it seems possible that some veneers have an inherent sensitivity to the manufacturing conditions which have been discussed, and are particularly liable to form non-gluing boards.

In order to test this idea, the adhesion of veneers which were just ready to be made into boards was tested, then the same sheet or batch of veneer was pressed at manufacturing temperatures and pressures without any bonding glue, and likewise tested for adhesion; and finally, the same veneers were made up into plywood either in the laboratory or at a firm's works. The results of these tests are given in Table 12.

TABLE 11. EFFECT OF BONDING GLUE ON GLUING PROPERTIES OF PLYWOOD

Ply	Urea-formaldehyde resin Hot-setting 100° C. 170 lb./sq. in.			PF paper film glue 140° C. 355 lb./sq. in.			UF resin to D.T.D. 484 Cold-set 130° C. 300 lb./sq. in.	Blood albumen 130° C. 300 lb./sq. in.	No. of tests	Type of test
	Max.	Mean	Min.	Max.	Mean	Min.				
Birch 1 mm.	1,170	1,008	600	1,130	913	640			48	No. 2
	1,130	1,029	700	1,130	904	450			48	No. 2
1 mm.					308		290	221	4	No. 5
3 mm.		5.7			6.6			6.8	4	No. 6

The glue joints were tested with filled urea-formaldehyde resin to D.T.D. 484.

Results represent failing loads in lb.

TABLE 12. RELATION OF PROPERTIES OF PLYWOOD TO THOSE OF VENEER FROM WHICH IT WAS MADE

	1 mm. A. series	1 mm. B. series	0.6 mm.	0.3 mm. (A)	0.3 mm. (B)	0.3 mm. (C)
Test type No.:	6	6	4	4	4	4
Veneer: as ready for ply	65	100	96	95	100	64
Veneer pressed without bonding glue	51	98	72	98	80	48
Plywood. Paper film glue	50	100	75	95 100	100 97	44
Plywood. Unfilled UF resin				100		
Plywood. Blood albumen				(85) 2 tests only		

Results represent average of six tests, quoted as percentage of the failing load of sanded controls. Filled UF resin to D.T.D. 484 was used for all test joints.

These results confirm the supposition that bad plywood springs from bad veneer; the only doubtful contrary result is that of the 0.6 mm. veneer reported in column 3, which made a worse board than would have been expected from its initial adhesion.

The next question which arises is why some veneers have this propensity to bad adhesion. There is no obvious property such as colour, lignification, or grain angle which is common to all bad veneers. Sections seen under the microscope show rather the same indistinct fuzzy outline as seen in the bad plywood boards (Section V (a) 1), but this is not very pronounced. A possible cause of bad gluing is the treatment the veneers receive to dry them when they come off the cutter wet. Rapid drying with pressure might give an impenetrable surface owing to the wood hairs being plastered down, like a wash-leather which has been wetted with water and rapidly dried. To test this, veneers were obtained wet from the peeler and dried in the laboratory by different methods; veneers from different commercial dryers were also tested. (See Table 13.)

TABLE 13. EFFECT OF METHOD OF DRYING VENEERS

Drying conditions	Beech sandwich (No. 4) Figures average of six tests	
	0.3 mm. veneer	0.6 mm. veneer
Schilde dryer	782	
Driad dryer		668, 646
Air dry	750	
Oven 80° C. Glued 3 days later	661	
Press at 10 lb./sq. in. 160° C. ½ hr.	691	

The results of these tests were inconclusive because all the veneers gave good joints failing in the wood.

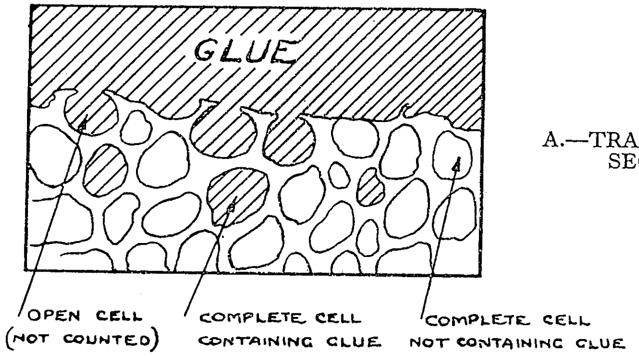
A general conclusion from the results reported in this section is that none of the usual manufacturing processes will by itself produce bad adhesion, but if a veneer is bad to begin with, all the various manufacturing processes through which it passes contribute something towards making it worse.

4. Measurement of effect of damage on penetration of glue

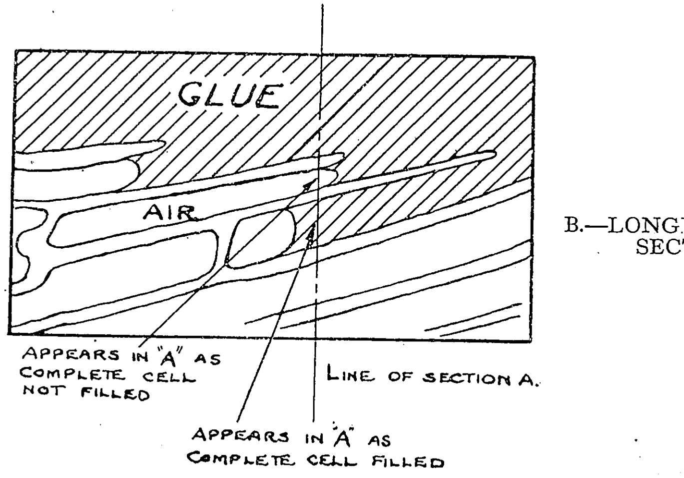
The most important effect of the mechanical and chemical damage already described is likely to be a decrease in the extent of penetration of glue into the wood. To assess the importance of these factors therefore, an attempt was made to measure the penetration of glue into samples of non-gluing and good gluing plywood to see if there was any difference.

The degree of penetration can be measured in two ways: (a) by cutting microscopic sections and counting the number of filled cells; (b) by watching the apparent increase in specific gravity of a sample which is hung from a balance and immersed in glue.

(a) The results obtained by the microscopic method are given in Table 14. The glue and the timber were differentially stained, and the number of cells touching the glue line with complete walls, were counted across the field, then the number of those containing glue were counted and the result reckoned as percentage of the available cells which the glue had entered. (See following diagrams.)



A.—TRANSVERSE SECTION



B.—LONGITUDINAL SECTION

This method ensures that account is taken only of the glue which has crossed the entrance of the wood capillaries. Four sections were cut on each joint and about ten counts taken on each section; the average of all these represents one percentage figure in the table.

TABLE 14. PENETRATION AND JOINT STRENGTH

Glue	1 mm. plywood bonded into paper plus glue				Remarks
	Sanded		Unsanded		
	Penetration	Average failing load for sheet	Penetration	Average failing load for sheet	Sanded by
UF resin with wood-flour filler	60%	1,144 lb.	90%	973 lb.	Sand blast. (See Section VII)
	100%	,,	78%	,,	
	38%	,,	33%	,,	
	66%	1,069 lb.	61%	831 lb.	Shot blast. (See Section VII)
	56%	,,	29%	,,	
	46%		60%		
	54%		51%		
	72%		54%		
PF resin	60%		44%		
Casein	7%		28%		
	9.5%		8.5%		
1 mm. veneer					
PF resin	27%		52%		Non-gluing plywood
1 mm. plywood					
	Glue rubbed in		Glue not rubbed in		
UF resin with wood-flour filler	92%		72%		All this ply was non-gluing.
	54%		29%		
PF resin	68%		55%		
Casein	8%		2%		
1 mm. veneer					
	Collodion stripped off		No treatment		
UF resin with wood-flour filler	18%		25%		For details see Table 4

Taking first the penetration of sanded and unsanded ply, we see that if we take the first eight figures together, the increased penetration of the sanded wood is just under 10% whereas the increase in joint strength is 12%. For the rubbed-in glue, the results are far more consistent, showing a difference of 40% in the penetration between the four rubbed and unrubbed joints. The scatter of the results is so wide, however, that in spite of the large number of observations (60,000 cells were counted), the correlation is not significant. A wide scatter is probably inevitable in this sort of observation, because of the small size of the units involved; there are about 100,000 cells opening on to the surface of a normal test piece of Type 2, and the failing loads obtained from this test piece have a standard deviation of about 20%; if we assume that the failing load of 1 sq. in. of glued area represents the mean of the contribution of all the individual cells, then the standard deviation for the value of any property of an individual cell should be very much greater than this.

(b) A gravimetric method of measuring penetration was used in order to check the microscopical results. The procedure was simply to record the apparent change in specific gravity of samples of wood immersed in glue, using a direct reading air damped balance and a stop watch. The results were calculated as volume percentage of the wood occupied by the liquid, assuming that the wood is completely hollow.

Percentage volume occupied

$$= 100 \times \frac{\text{Initial wt. of liquid displaced—new wt. displaced}}{\text{Initial wt. of liquid displaced}}$$

An unfilled UF resin glue with an ammonium chloride hardener was used in the first place, but it was found that the high viscosity, together with a tendency for the glue to set rapidly in such a large bulk, made accurate measurements impossible. Glycerine is more manageable and has practically the same surface tension (62, as compared with 63 dynes/cm.) and only a slightly lower viscosity. The curves for the penetration of birch veneers by UF resin and glycerine were found to be similar, so the experiments on non-gluing and on sanded plywood were done with glycerine (see Fig. 14). The end grain and the opposite face of each specimen were waxed, so that only the surface with known adhesive properties was exposed to the glycerine. Fig. 14 shows the curves for two good and two non-gluing plywood surfaces; for one pair there is no significant difference between the two curves, for the other the good surface shows faster penetration than the bad. The slope of the lines is not important because it represents rate of penetration; for fairly deep penetration this depends on the diameter of the tubes and on the viscosity of the glue, whereas in actual practice we are concerned with very shallow penetration in which viscosity is not important (see V (b)). The value of the ordinates is, however, important, as indicating differences in the number of cells penetrated.

(b) Surface Tension and Viscosity of the Glue

Apart from the size of the capillary spaces and the shape of their openings, the most important factors governing the penetration of a liquid into a porous solid are the viscosity and surface tension of the liquid, and the advancing angle of contact between the liquid and the solid. The effect on penetration of varying these properties was therefore investigated.

Surface tension

Penetration is favoured by a low surface tension, but most synthetic resin glues were found to have a surface tension of about 60 dynes/cm. which is fairly high (cf. water 74, alcohol 22). It was thought that this might change as the glue set, and so hinder or help penetration. Therefore, measurements of the surface tension were made at different stages in the setting of resin glues.

The surface tension was measured by finding the pressure on a water manometer which was required to blow a bubble of air in the glue. Provided the bubble is formed slowly, the surface tension is equal to $P \frac{1}{2} r$ where r is the capillary radius and P the manometric pressure, and neither viscosity nor angle of contact need be taken into account. Fig. 15 shows that the surface tension of a setting glue remains nearly constant, until a certain high viscosity is reached, when it appears to increase suddenly to values too high to measure on the apparatus. The high viscosity does not interfere with the measurement of surface tension until the glue has practically set. This can be checked by the temperature coefficient, because temperature affects the viscosity of glue greatly, but its surface tension

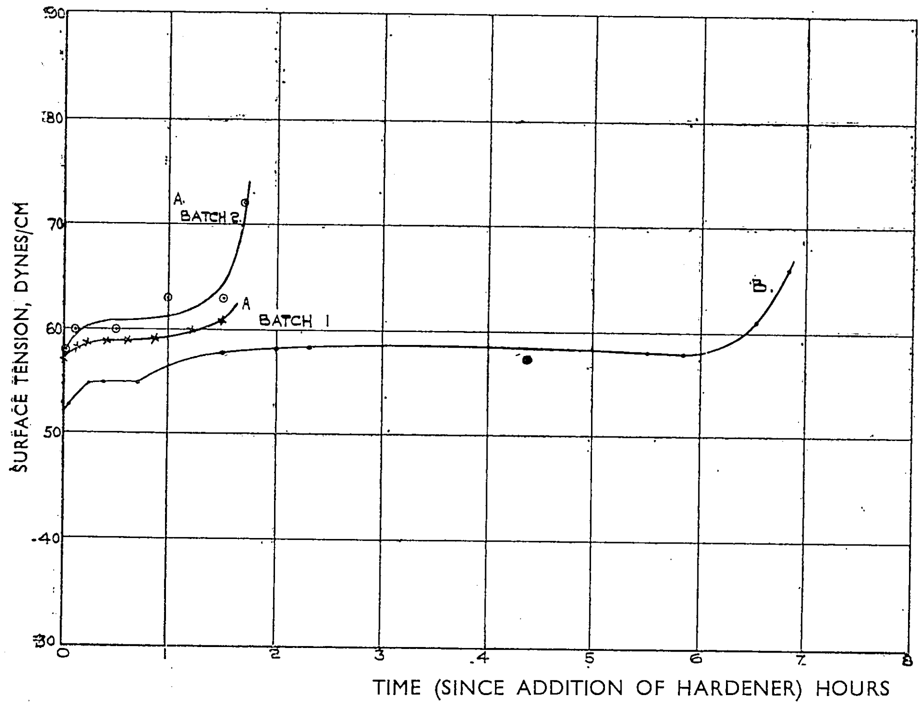


Fig. 15. SURFACE TENSION OF GLUES

Density of Glues

A. Unfilled UF resin to D.T.D. 335 + 10% rapid hardener.
sp. gr. (d) freshly mixed = 1.44
sp. gr. (d) set solid = 1.25

B. PF resin to D.T.D. 484 + 13.5% hardener
sp. gr. (d) freshly mixed = 1.23
sp. gr. (d) set solid = 1.28

Formula Used

$$\sigma = \frac{gr}{2}(\rho h - xd)\ 0.75$$

where σ = surface tension
g = 980 dynes
r = 0.0158 cm.
ρ = 1 for water manometer
x = 0.5 cm. depth
d = density of liquid

should not alter more than 2 or 3 dynes/cm./10° C. The results in Fig 16 show that water has a coefficient of 2.5 dynes/cm./10° C. and typical UF and PF glues to D.T.D. 484 about 3.5 dynes/cm./10° C. if taken over a reasonable range. These results confirm the reliability of the method adopted for measuring surface tension, and justify the conclusion that the surface tension of synthetic resin glue does not change as the glue sets.

Viscosity

In general, penetration of a liquid is hindered by high viscosity providing the other factors are constant. The results in Table 15 show that over the range of viscosities which are possible with synthetic resin glues, there is no correlation between viscosity and joint strength.

TABLE 15. THE EFFECT OF HIGH VISCOSITY OF GLUE
(Urea-formaldehyde with filler to D.T.D. 484)

	Normal viscosity	High viscosity desiccated	High viscosity stale, setting
$\frac{1}{16}$″ ply, non-gluing	3.94(4)	4.52(4)	
0.8 mm. ply, not badly non-gluing	3.2(6)	3.5(6)	3.8(10)

Test type No. 6. The figures in brackets are the number of tests performed. The figures represent average failing loads in lb.

(c) Emulsification of Glue

If a series of joints in sanded and unsanded plywood is made up with a urea-formaldehyde resin to D.T.D. 484 containing a wood-flour filler, and the thickness of the glue line gradually increased, it will be found that there is a critical thickness, above which joints made with either sanded or unsanded plywood fail at the same low load and both are stripped failures (Table 15). This occurrence of stripped failures in joints between sanded plywood in which there is a thick layer of glue is something distinct from the forms of adhesion failure discussed so far. It is always accompanied by a whitening of the glue, which has a chalky consistency and is more friable than usual. The white appearance is due to emulsification of the resin. Liquid urea resin glues are partly soluble in water, but as they set they become less soluble, and if excess water cannot escape from the glue line before the glue hardens, the water separates out as minute droplets, and an emulsion is formed. Emulsified resins do not feel sticky to the touch, and have no adhesive power, probably because the emulsion breaks down locally when they are brought into contact with a hydrophil surface, so that the water spreads as a continuous film between the resin and the substrate.

Stripped failures due to emulsification of synthetic resin glues are most common in joints between two plywood surfaces. If $\frac{1}{8}$″ beech veneers are joined with a very thick layer of filled UF glue to D.T.D. 484, only the centre is emulsified; the glue touching the wood is clear and dark coloured because the water has escaped and the glue is homogeneous. Such joints fail either in the wood or in the centre of the glue line, and the breaking load is barely affected by the thickness of the joint (Table 16).

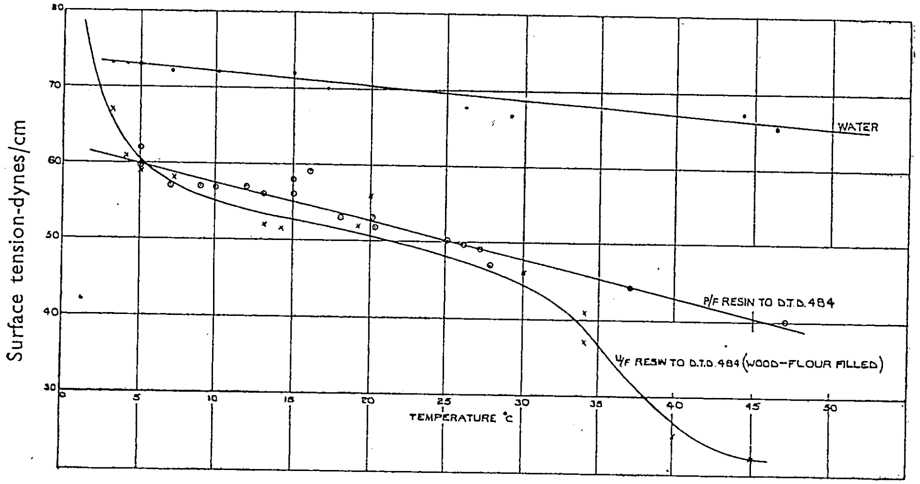


Fig. 16. VARIATION OF SURFACE TENSION OF GLUES WITH TEMPERATURE

TABLE 16. THICKNESS OF GLUE LAYER

	Thickness of glue layer						Type of test	Remarks
	Close contact		0.03 in.		0.06 in.			
	Sanded	Unsanded	Sanded	Unsanded	Sanded	Unsanded		
Birch Plywood 0.8 *mm.* A. Urea-formaldehyde resin to D.T.D. 484 (wood-flour filler)	1223	880	1213	1133	740		No. 3	All joints below 850 lb. gave stripped failures
No. of tests	16	24	18	16	13			
B. Casein		421				420	No. 3	Many failures due to frothy glue, no stripped failures
No. of tests		6				6		
Beechwood slips ⅛ *in.* UF resin as 'A' above				796		762	No. 3	All failures in the wood or in the glue itself
No. of tests				6		6		
Casein as 'B' above				606		422	No. 3	Failures at 0.06" due to foamy glue, no stripped failures
No. of tests				6		6		

All figures represent mean failing loads in lb. of six tests.

In non-gluing plywood, the effective area of contact between glue and wood is reduced (V (a) 1) and so the escape of water is made more difficult and the probability of emulsification increased. This will make the gluing properties of the plywood worse. When the wood is very dry (V (d)) the penetration of the glue is poor, the effective area of contact is small, and the centre of the joint emulsified.

Gap-filling glues to D.T.D. 484 which contain a filler emulsify much more easily than the non gap-filling glues (D.T.D. 335A), probably because the particles of filler act as nuclei around which water can collect. Casein from its chemical nature is unlikely to form an emulsion, and it is found in practice that casein-glued joints show no critical thickness of glue layer at which their strength suddenly drops (Table 16), although there is a steady deterioration due to increasing vacuolisation and weak foam structure.

If a spruce/plywood joint made with a thick layer of UF resin filled with wood flour is broken about 17 hours after being made up, it will give a stripped failure with severe emulsification; 24 hours later, however, the exposed glue surface will have lost its white, chalky appearance and be no longer emulsified. The most probable explanation of this change is that the excess water which formed the disperse phase of the emulsion has escaped, and the resin is still sufficiently plastic to fill up the spaces. If the same joints are not broken until two or three days after being made, the chalky appearance does not disappear when the glue surface is exposed, but becomes more pronounced with age; the resin has become hard, so that when the water escapes, the resin will not flow into the empty space. The spaces once occupied by water therefore become filled with air, and the chalky appearance is intensified.

It seems likely that an emulsified glue layer may sometimes recover in the way described above without the joint having been broken. A joint in which this happened would not necessarily regain strength, although the glue might appear completely translucent and homogeneous in the broken specimen, because the separation between resin and wood due to the water film may still persist.

Glue does not emulsify unless the wood is either very dry or very wet (see V (d) and Table 17). Exact comparisons are difficult to make because the mechanical properties of the wood vary with its moisture content.

TABLE 17. EFFECT OF THE MOISTURE CONTENT OF WOOD UPON THE ADHESION OF FILLED UREA-FORMALDEHYDE RESIN GLUE TO D.T.D. 484

Wood in equilibrium with R.H. (% at 25°C.)	0	30	70	75	95	98	100
1 mm. veneer, Test type 4	271	318	252				430
$\frac{3}{64}$" ply, Test type 2		280	240	315	250 260	290	280
0.8 mm. ply, Test type 2		420	400	310			

Figures represent mean failing load in lb. for batches of either 6 or 8 joints.

(d) Temperature and Humidity

It has been suggested that dehydration of the wood caused by overheating in the press is the sole cause of stripped failures and that the non-gluing condition of plywood could be cured by restoring the original moisture content. In Report No. 2 it was shown that dipping the plywood in water after pressing does not improve the gluing properties.

Heating wood to pressing temperatures does cause a temporary deterioration of its gluing properties. Birch veneers $\frac{1}{16}''$ thick were heated at 160° C. for 10 minutes without any pressure, and glued with UF resin glue as soon as they were cool. The average failing load was 284 lb. for a $\frac{1}{2}''$ overlap joint (Test type 5) compared with 436 lb. for similar unheated strips. When the wood was left at room humidity for four days after heating, the average failing load rose to 363 lb. from which it appears that restoration of moisture content would eventually cause the heated and unheated veneers to fail at the same load. It is probable that the effect of heating is due to moisture loss and not to chemical changes induced by the high temperature, because veneers dried to constant weight over calcium chloride before gluing had their joint strengths reduced by 34%.

All these dry joints failed between the wood and the glue, with a typical stripped failure. The strength of the joints was slightly improved by sanding the wood, and restored to normal by rubbing the glue into the wood. Thus the effects of heating appear to be largely a matter of penetration. This can be demonstrated by cutting microscopic sections of tension-fractured end grain which has been dipped into a cold-setting UF resin glue after being in the one case desiccated and in the other of normal humidity. From Figs. 17 and 18, it will be seen that in the unheated wood the glue has penetrated about 0.4 mm. and in the heated about 0.1 mm. The poor penetration is probably due to the dry capillary walls so dehydrating the advancing glue column that it forms a "skin" which retards it. The decreased penetration will have the effect of diminishing the surface of contact between glue and wood, and so making further moisture exchange more difficult, and it is a paradoxical fact that extremely dry wood will cause the glue to emulsify.

The ill-effects of this lack of penetration are intensified by tensile stresses set up in the joint by the swelling of the wood in contact with the glue line. In extreme cases the joint is bent apart and the edges gape.

In conclusion, the heating which plywood undergoes during its manufacture can cause a temporary tendency to stripped failures which disappears as soon as the wood regains its normal moisture content. This is independent of permanent non-gluing properties and is not likely to cause much trouble in practice as long as plywood is kept for some time in store after manufacture.

(e) Shrinkage of Glue and Swelling of Wood

It has been pointed out that glued joints may fail from the effects of shear stresses produced by unequal thermal expansion of the bonded and bonding materials. It is unlikely that atmospheric temperature changes could produce any effective stresses in glued wood joints, but the same general argument can be applied to the stresses set up by swelling of the wood by moisture, or the contraction of the glue as it sets, and these factors might produce sufficient shear stress at the surface between glue and wood to make a slightly defective joint much worse.

Moisture

It is very difficult to find out what effect the swelling of the wood by moisture has upon joint strength, because in the first place the swelling is anisotropic, and secondly, the moisture makes mechanical changes in the wood of the test joint. Gross warping of the wood caused by unequal swelling may set up tension in the glue in a direction normal to the plane of the joint. A spruce laminated spar has been seen which failed in this way.

Contraction of the glue

The magnitude of this contraction is shown in Fig. 21, which represents the percentage reduction of the volume of 9 ml. cylinders of casein, urea and phenolic glues. Cylinders of 18 ml. and 25 ml. were also measured, and showed that the

FIG. 17. PENETRATION OF UF GLUE TO D.T.D. 335 INTO SPRUCE OF NORMAL HUMIDITY. (Tangential Section)
Magnification x 170.

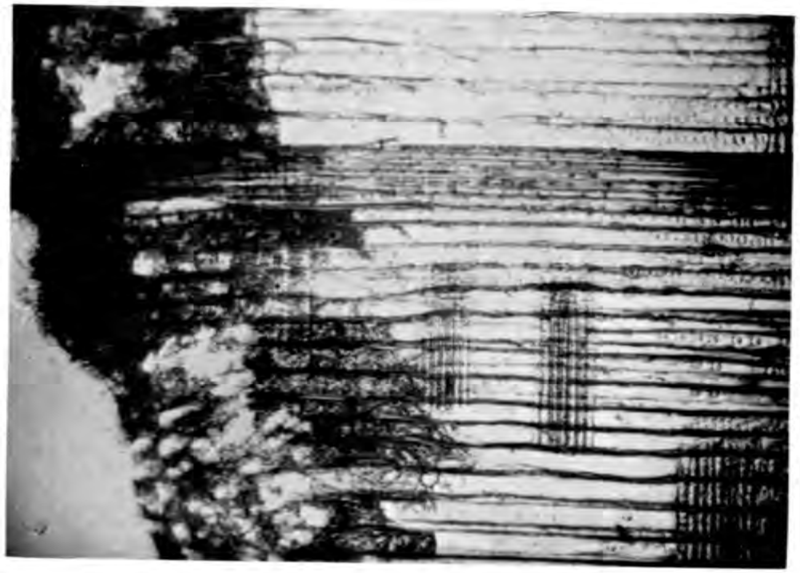


FIG. 18. PENETRATION OF UF GLUE TO D.T.D. 335 INTO DRY SPRUCE (Radial Section)
Magnification x 170.

FIG. 19. CRAZING, SANDED JOINT. UF GLUE TO D.T.D. 335
Magnification x 2.

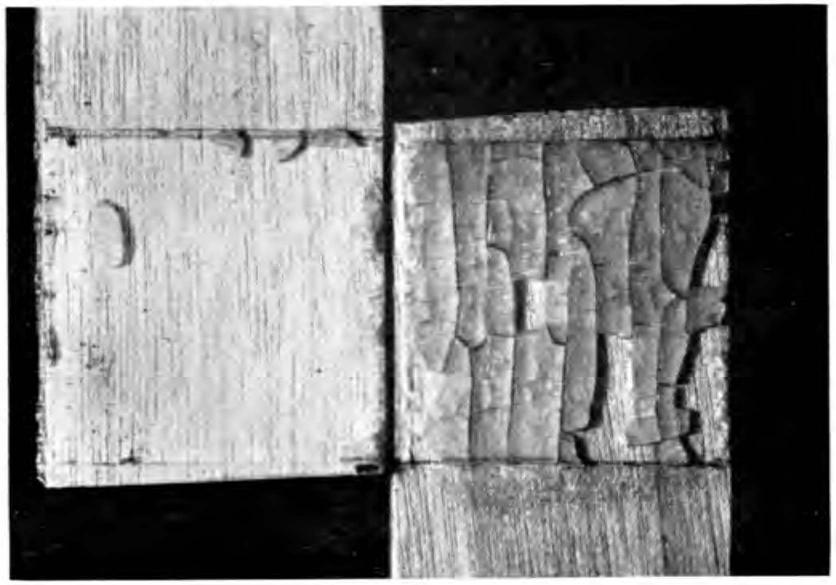


FIG. 20. CRAZING, UNSANDED JOINT. UF GLUE TO D.T.D. 335
Magnification x 2.

rate of contraction decreased and the final volume was relatively larger as the volume of the glue increased. From this one might expect that the amount of contraction taking place in the small volume of glue in a joint must be relatively greater than that recorded in the graph for lumps with a volume of 9 ml. According to these results, after 3 days a casein glue contracted by 38% of its original volume; an unfilled urea-formaldehyde resin by 12%, a wood-flour filled glue to D.T.D. 484 by 3%, and a cold-setting phenol-formaldehyde resin by 2%.

There are two ways in which shrinkage of the glue could affect the joint strength. (1) Contraction in the same plane as the joint would cause a shearing stress along the glue-wood interface. (2) Unequal contraction of some resin glue causes crazing, so that the bonding material is weakened by cracks. In protein glues and in resin glues covered by specification D.T.D. 484 there is no crazing but in the non gap-filling glues to D.T.D. 335A the two are almost inseparable.

Uniform contraction

Thick casein joints between spruce and glass show the effects of volume contraction; the adhesion to the glass is excellent, but the glue at the edge of the joint dries and contracts more than that in the centre, so that the glass is bent until it cracks. Glues to D.T.D. 335A show the presence of shear stress between the glue and the wood by not crazing much when the adhesion to the wood is poor and slip is possible (see Fig. 20) and crazing very badly when little slip is possible owing to good adhesion produced by sanding the joint (see Fig. 19).

Crazing

Stripped failures are not usually associated with cracking or crazing of the glue, because crazing becomes less serious as adhesion becomes worse. When the glue in a joint crazes, most of the cracks are normal to the wood surface, so that they divide the glue into pillars or blocks between the faces of the joint. In plan view these are frequently rectangular, arranged in straight rows down the grain with their long sides at right angles to it. When the joint is stressed in shear, failure occurs partly between the top of each block of glue and the wood and partly by secondary cracks through the blocks of glue. The secondary cracks are conchoidal, and in their most typical development they are more or less circular in plan, and a pointed dome-shape in elevation, so that they cause a fragment shaped like an acorn to drop out of the middle of each rectangular block of glue.

It seems likely that the primary cracks are due to the outside of the glue mass shrinking relative to the inside, whereas the secondary conchoidal cracks are due to the inside of the blocks so isolated, shrinking relative to the outside.

In conclusion, stripped failures are not necessarily connected with crazing. Bad adhesion may be aggravated by shear stresses due to shrinkage of the glue in the plane of the joint, but it is extremely difficult to assess the importance of this, because most of the contraction takes place while the glue is still plastic and can relieve itself of stress by flowing.

VI. General Discussion

The evidence so far available is consistent with the idea that the basic cause of bad adhesion and stripped failures is a decrease in the amount of penetration of the wood by glue. It is important to note that within certain limits, the frequency with which glue penetrates wood capillaries is more important than the depth of penetration.

That it is the relative number of capillaries penetrated rather than the depth of penetration which is effective, is borne out by the examination of types of failure

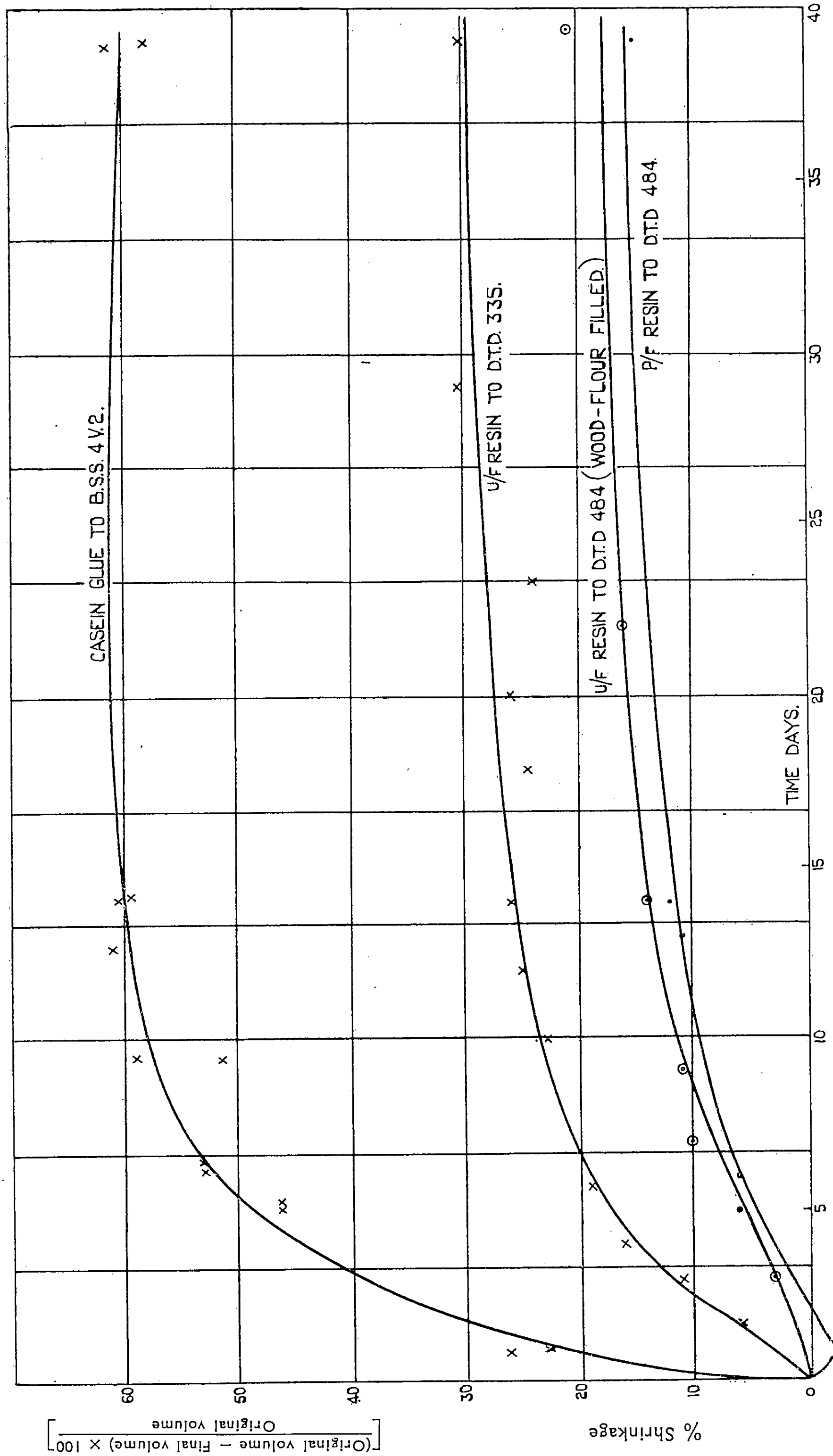


FIG. 21. CONTRACTION OF GLUES ON SETTING

intermediate between typical stripped failures and gross wood breaks. If depth of penetration was the predominant factor, one would expect that with increasing penetration, a thicker layer of wood would be left on the surface of the glue in a broken joint; instead of this, one finds that the typical intermediate condition is to have isolated fibres left adhering which are more frequent the better the joint.

The factors which have been suggested as responsible for decreasing local penetration are all of a nature to act in a discontinuous, all-or-nothing way; except perhaps for desiccation of the glue by extremely dry wood (V (d)), they determine whether or not the glue will enter a capillary at all, rather than its rate of penetration once it has entered. The transition between the local behaviour of good and non-gluing plywood is made still more abrupt by the effects of bruising of the ends of the wood fibres. Very shallow penetration cannot have any effect in increasing joint strength, because adhesion is only to the crushed ends, which are weak; but any penetration deep enough to reach the sound wood beneath will result in a fair proportion of wood failures.

The sequence of causes leading to typical case-hardened stripped failures may be summarised as follows:

1. (a) The number of cells penetrated by glue is decreased because the ends of some are blocked by crushing of the walls or by debris. (See V (a) 1.)
   (b) This effect may be intensified by the results of impregnation of the ends of the cell walls with resin. (See V (a) 2.)
2. The crushing also reduces the surface area which is available without penetration. (See V (a) 1.)
3. What surface is available is of little value because it is broken or bruised and has little strength. (See V (a) 1.)
4. The decrease in the area of contact between glue and wood makes it more difficult for water to escape from synthetic resin glues, and leads to emulsification. (See V (c).)

VII. Remedies for Case-Hardening

From the results in Section V (b) it is obvious that bad gluing properties cannot be avoided by any easy modification of the processes of manufacturing plywood. A cure by chemical treatment would be easier to apply on a large scale than any process of mechanically sanding the surface.

(a) Chemical Treatment

If the suggestions for the causes of stripped failures are correct, it follows that no chemical treatment of the wood is likely to remove its non-gluing surface. This has so far proved to be the case.

Rehumidification

At the time when overheating and desiccation of the wood were thought to be the cause of stripped failures, it was proposed to cure the defect by dipping the sheets in water after they left the press. Mere dipping was shown to be ineffective in Report No. 2, but it was suggested that thorough soaking of the plywood, followed by controlled drying, might be more effective. This was investigated on a series of sheets which were all soaked in hot water after manufacture, and then dried in an air-conditioned plant. The tests (see Table 18) showed that there was no significant difference between plywood treated in this way and plywood which had not even been dipped; the treatment is useful only in removing internal stresses and so producing a sheet which lies flat.

TABLE 18. TREATMENT BY IMMERSION

Untreated			Dipped			Mean difference	No. of tests	Type of test
Min.	Mean	Max.	Min.	Mean	Max.			
600	918	1,165	810	1,002	1,160	+ 84	24	No. 2
860	1,050	1,300	710	1,002	1,150	— 48	24	,,
740	918	1,130	640	910	1,140	— 8	24	,,
450	830	1,030	760	955	1,140	+125	12	,,
1,020	1,132	1,280	830	1,050	1,260	— 82	24	,,
380	526	710	520	681	780	+155	18	No. 1
640	687	770	650	695	750	+ 8	6	,,
500	525	700	480	508	600	— 17	6	,,
540	546	550	500	561	630	— 54	6	,,

(Each horizontal line refers to a separate sheet of plywood).

Ammonium hydroxide

It has been claimed that treatment of plywood with alkali in the green veneer, and to a lesser extent in the finished board, dissolves away the surface resins and results in a more supple product; if the resins were removed the wood might glue better (see V (a) 2). Veneers and plywood were soaked overnight in 15% NH_4OH and dried in warm air before gluing. Test results are given in Table 19.

TABLE 19. AMMONIUM HYDROXIDE TREATMENT

Test type No. 4. UF glue to D.T.D. 484 with wood-flour filler. Results show average failing load of five tests in lb.

Non-gluing wood				Good wood			
Plywood		Veneer		Plywood		Veneer	
Untreated	Treated	Untreated	Treated	Water dipped	Treated	Water dipped	Treated
351 All case-hardened	370 Mostly case-hardened	480 All case-hardened	525 Few case-hardened	668 Wood failure	606 Wood failure	715 Wood failure	668 Wood failure.

The ammonia treatment makes no significant difference to the joint strength.

Wetting agents

Stripped failures are partly caused by poor penetration of the glue into the wood and it might be expected, therefore, that if it were possible to lower the angle of contact between the glue and the wood from its usual figure of about 15° to 0°, better penetration, and so better adhesion, would be obtained. This might be done by lowering the surface tension of the glue (which is usually about 60 dynes/cm.) by the addition of wetting agents, although on detailed consideration important objections appear.

The essential property of a wetting agent is that it shall have in different parts of the molecule both water and oil soluble groups whose affinity for their respective solvents is about equally balanced. Molecules of this kind will not entirely dissolve in either oil or water, but will collect at the interface; at a water-air interface the oil-soluble groups will be directed towards the air so that the surface is effectively "oily" and has a correspondingly low surface tension.

The water-soluble group in most wetting agents is an acid radical, and as synthetic resin glues are themselves strongly acid they will tend to reject the water-soluble group, which will become attached to the wood. The wetting agent will therefore arrange itself with its water-soluble groups towards the wood and its oil-soluble groups projecting and instead of making the wood more easily wetted by glue it may be expected to waterproof the surface and make penetration more difficult. Wetting agents are available in which the water-soluble group is basic; these might orientate with the water-soluble group toward the glue, but then the affinity of the oil-soluble group for the wood becomes the limiting factor. The results of experiments with various wetting agents agree with this theory; soaps, cetyl alcohol, "T.R.O.", "Teepol" and sulphonated lorol, either applied to the wood or mixed with the glue, all make adhesion worse, and give rise to typical stripped failures.

In phenolic glues, the hardener usually acts as a wetting agent which prevents emulsification of the glue; from what has been said above it appears, however, that it must not be a very efficient wetting agent or it may decrease the joint strength. This is borne out in practice; in one make, for example, the air-glue surface tension is only reduced by addition of the recommended amount of hardener from 63 to 60 dynes/cm.

From the figures given in Table 20 it will be seen that the only wetting agents which have any beneficial effect on the joint strength are those which do not cause a very great decrease in the surface tension at an air-glue interface. It seems possible that glues to D.T.D. 484 might be improved in some instances if their tendency to emulsify were diminished by a judicious addition of a mild wetting agent, but in general the use of wetting agents does not offer much hope of a cure for bad adhesion.

TABLE 20. WETTING AGENTS

Urea-formaldehyde resin with filler (D.T.D. 484) used throughout.

Non-gluing plywood. Test type No. 6.

Wetting agent (2% $\frac{w}{w}$ of mixed glue)	Failing load, lb./in. Mean of 10 tests	Type of failure	Surface tension glue-air. By bubble method in dynes/cm.
Nil control	3.2	All stripped	61
Perminal 2. I.C.I.	3.8	All wood	59
Calsolene oil HS. I.C.I.	3.5	2 wood 8 stripped	49
Irgapol	3.0	All stripped	41

Average veneers. Test type No. 4.

Wetting agent (10% $\frac{w}{w}$ of mixed glue)	Average of 6 tests	Type of failure	Surface tension glue-air. By bubble method in dynes/cm.
Nil control	637	4 wood 2 stripped	61
Perminal W. I.C.I.	780	All wood	58
"T.R.O." 83%	627	All stripped	45

Non-gluing ply. Test type No. 4.

	Average of 4 tests		
Nil control	612	All stripped	61
($\frac{w}{w}$ of mixed glue)			
10% Perminal W.A. I.C.I.	544	2 glue 2 stripped	—
5% ,,	548	All stripped	53
2% ,,	523	All wood failures	—

(b) Mechanical Remedies for Bad Adhesion

Bad adhesion can be cured with some certainty by sandpapering the wood by hand with a medium grade of paper (Report No. 2). It is, however, difficult to distinguish between lightly-sanded and unsanded wood by either look or feel, so that there is no easy check upon whether the operator has actually sanded the joint before assembly or not; in any case, hand sanding is slow and expensive, and it was therefore required to find a mechanical method of sanding which could be applied to all plywood before it was issued to the manufacturer.

Overhead belt sanding

In this process a continuous belt of sandpaper is mechanically dragged over the surface of the wood, pressure being applied by a pad. The pressure is controlled by the operator so that skill is required for satisfactory results.

TABLE 21. RESULTS OF BELT SANDING

Type of test	No. of tests	Unsanded	Hand sanded in the laboratory	Machine sanded
No. 2	6	716	842	787*
No. 3	7	441	—	464
No. 3	12	340	—	605*

Results are means in lb. *Operator supervised.

The results in Table 21 show that when the operator was supervised the process was about 76% as efficient as hand sanding, but where there was no supervision it only slightly improved the adhesion of the wood. Therefore, belt sanding cannot be considered very much more reliable than hand sanding under factory conditions.

The machine can only treat one side at a time; if plywood is issued with only one side sanded, then all asymmetrical-shaped parts become right or left-handed and more drawing numbers are required; if both sides are treated, the time required is excessive (about 1½ minutes per sq. ft.) and the decrease in thickness is more likely to be serious.

Circular wire brush

This is a mechanically-operated brush, which gives fairly satisfactory results, and does not remove an excessive amount of wood. In preliminary trials, however, it was found that it did not give quite such consistently satisfactory results as the sand-blast methods, and it was not developed further. The results are summarised in a frequency graph (Fig. 23, No. 2) where the shaded portions are the untreated wood, and the thick lines the treated.

Airborne sand or shot-blast

In these processes an abrasive is blown on to the wood under an air pressure of 5-7 lb./sq. in. It will be seen from the frequency graphs in Figs. 22 and 23 that both shot and artificial sand are fairly efficient, but that if anything, artificial sand gives the most consistently satisfactory results. The results obtained from the treatment by artificial sand compare favourably with those obtainable after careful hand sanding.

Centrifugally projected abrasives

This process is essentially similar in effect to the airborne sand-blasting, but centrifugal force is substituted for compressed air. The machinery is simpler

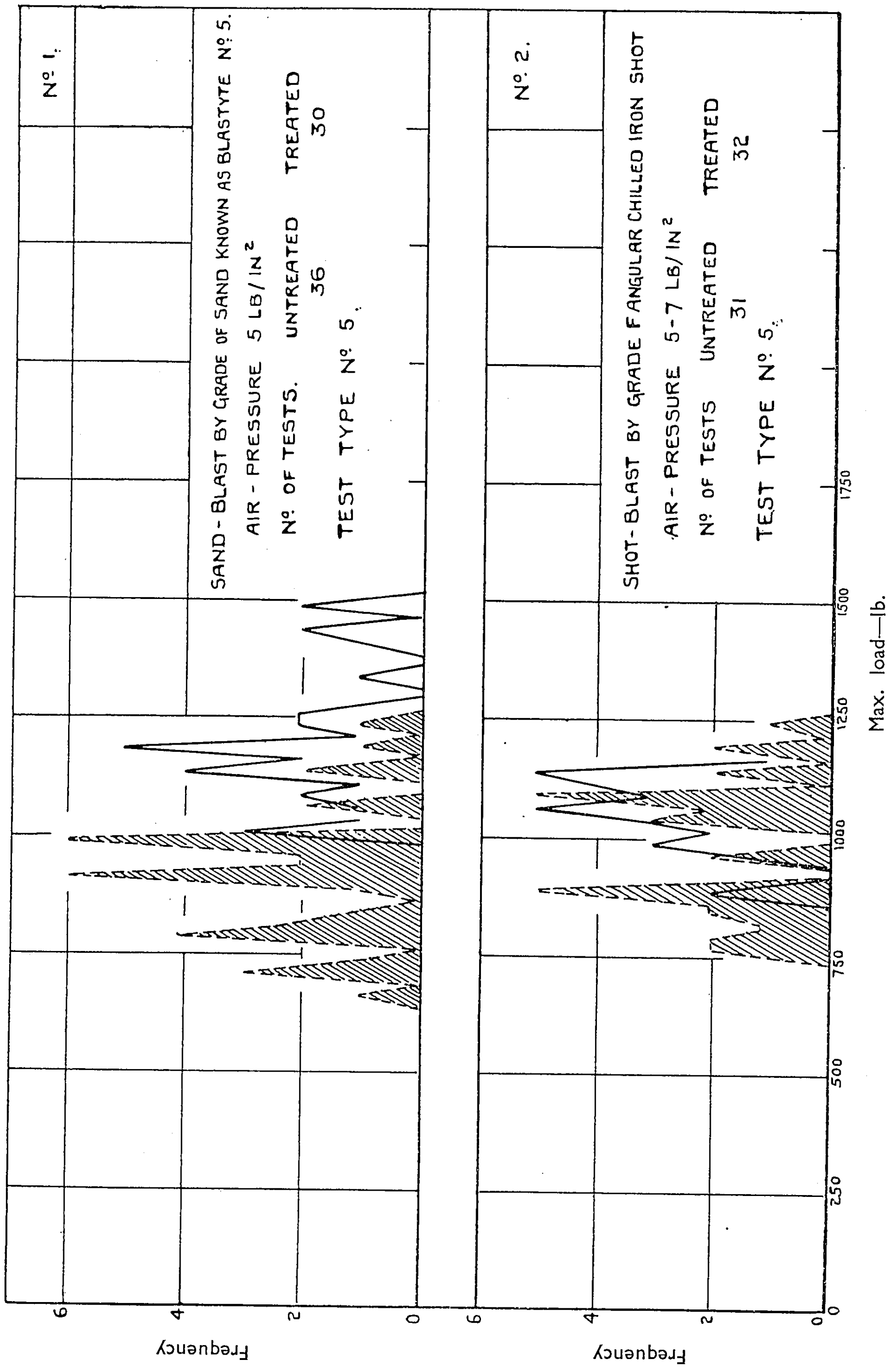


FIG. 22.

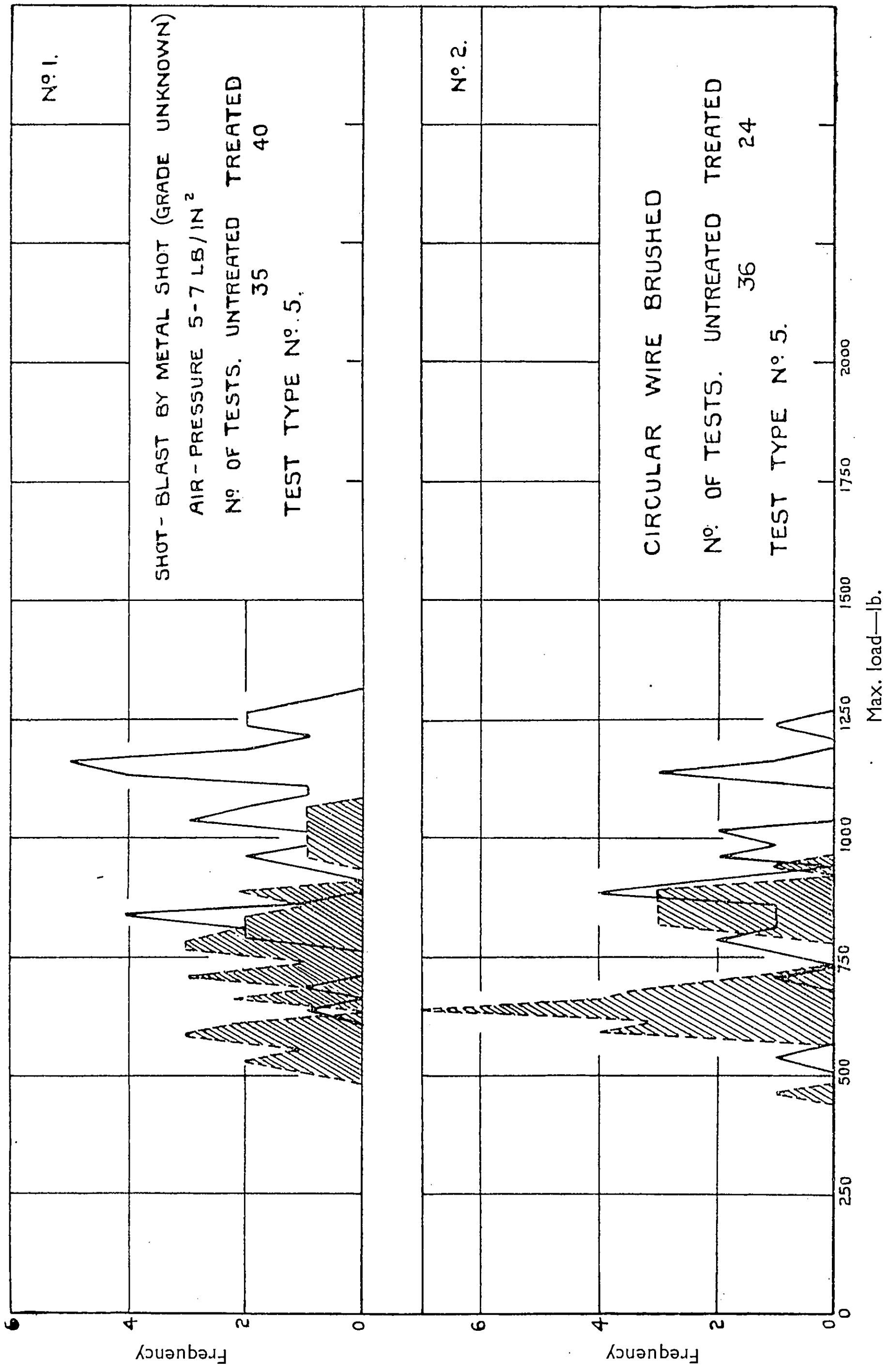


FIG. 23.

to construct and its output of sanded wood greater than that of the air-blast plant. The results on non-gluing plywood are quite satisfactory, and it is anticipated that the process will be further developed.

Conclusions

With either the centrifugal or the simple pressure sand-blast processes, the thickness of wood removed is negligible; the decrease in thickness which results from treatment on both sides is less than 0.001″. The apparatus can be arranged to treat both sides of the board at the same time, and the time required is about one minute for both sides of a sheet of 100 sq. ft.

We conclude that non-gluing of plywood can be effectively cured by treating the wood with a suitable abrasive projected either by centrifugal force or compressed air. Such a treatment would be suitable for general application to all plywood before it is issued to the aircraft manufacturer.

VIII. Appendix

The following are examples of accidents or defects which appear to be wholly or partly caused by "case-hardened" glue failures. (The numbers appearing against the type of aircraft in which defects appeared, refer to the R.A.E. tests and bear no relation to specific types of aircraft.)

*Trainer V.*3507

Defect found during inspection. Upper skin (0.8 mm. 3-ply) stripped away from large part of main plane (ribs 0-4 inclusive). (Casein).

*Trainer T.*1043

Structural failure in air. Attachment of upper skin of tail plane to spar flange. (Casein).

*Trainer V.*3845

Structural failure in air. Attachment of web of tail plane spar. (Casein).

*Trainer III W.*8852

Structural failure in air during test aerobatics; defective gluing of main plane skin to ribs contributory factor. (Synthetic resin cement. Separate application of resin and hardener.)

Glider

Defects appeared during manufacture of tail fins; plywood (Guarea) fell off underlying structure as soon as glue dried. (Casein).

Glider

Defects appeared during manufacture of fuselage frames; plywood peeled off spruce members when glue set. (Synthetic resin cement. Resin mixed with hardener before application.)

*Reconnaissance aircraft A.X.*542

Defects found during repairs. Joint between main plane skin and bottom spar flange (Casein). Joint between main plane front spar web to flanges. (Synthetic resin cement. Separate application.)

Reconnaissance aircraft

Category E aircraft from Salvage Department of parent firm. Repair joint between spar web and flanges. (Casein).

*Reconnaissance aircraft A.X.*501

Defects found during repairs. Spar webs to flanges. (Synthetic resin cement. Separate application.)

Reconnaissance aircraft at Cranage

Some cases of upper main plane skins coming away from stringers. (Casein).

*Reconnaissance aircraft D.J.*477

Defects found during repair. Patches of bad adhesion between main plane skin and stringers of ribs. (Casein).

Fighter rudder

Defect found during inspection. Bad adhesion of plywood skin to rib had aggravated the effects of faulty design (inadequate glued area). (Casein).

Trainer aircraft in South Africa

Complaints received that in some cases joints between plywood and spruce have stripped away clean, leaving glue on spruce. Probably due to "case-hardening." (Synthetic resin cement. Separate application.)

Petrol tank

Defect found during test. Prototype moulded plywood 30-gallon drop tank for Spitfire. Failure of joint between internal framework and shell. (Hot-setting synthetic resin cement.)

Glider

Defects found during inspection. Several instances of stringers coming away from skin of fuselage. (Synthetic resin cement. Separate application.)

Reconnaissance aircraft tail plane, Serial No. 164761

Rejected by inspection staff of manufacturing firm. Case-hardening of skin or rib booms. (Synthetic resin cement.) (Very thick glue lines, emulsification.)

Report No. 4

Tests to Determine the Effects of Various Types of Adhesives on the Final Shape of Laminated Bends

(Based on Ministry of Aircraft Production Scientific and
Technical Memorandum No. 26/45, November, 1945)
by W. C. Stevens and N. Turner, Department
of Scientific and Industrial Research

U.D.C. No. 668.3 : 674-419

Abstract

Tests were carried out on cold-setting glues including urea-formaldehyde and phenol-formaldehyde synthetic resin glues. The influence of the adhesives on the laminated bentwork, where accuracy of shape was essential, was investigated. Tabulated results are given. In an appendix technical considerations of the movement of bends resulting from changes in moisture content are given.

Contents

Illustrations

I. Introduction

Investigations carried out at the Forest Products Research Laboratory concerning the movement of laminated bends had shown that any factor which influenced the moisture content of a bend, such as type of glue, number of glue layers, etc., influenced also the subsequent shape of the bend after the setting of the glue.

Since these investigations were made, a considerable number of new cold-setting glues, notably of the urea-formaldehyde and phenol-formaldehyde synthetic resin types, have been developed and used in the production of laminated bends for aircraft and furniture parts.

The investigation described here was carried out primarily to supplement data already obtained on the influence of adhesives on the final shape of bends and also to determine which of the glues commonly used in this country were the most suitable for laminated bentwork when accuracy of shape was an essential requirement.

II. Details of Glues, Setting Times and Glue Spread

The majority of the glues tested were, at the time the schedule of tests was prepared, approved to specifications D.T.D. 484 and D.T.D. 335A. Five different types of glues were tested, namely, gap-filling and non gap-filling urea-formaldehyde resins, phenol-formaldehyde, animal and casein. Several proprietary makes of each of the resins were tested, comprising a total of 15 different adhesives. Furthermore, where manufacturers recommended more than one method of application such as, for example, single or double spread, separate or mixed application, alternative hardeners and mixes, etc., tests were sometimes made on each of the recommended methods.

The glues were all obtained direct from the manufacturers and were made up in strict accordance with issued instructions.

In Table 2 details are given of all the glues and of the various bonding procedures employed.

The spread in the majority of tests was 6 lb. per 100 square feet per single glue line and when the double-sided spread was used, this quantity of glue was applied to each of the two surfaces to be bonded. Details of the spread used for the remaining glues are recorded in Table 1.

TABLE 1

Adhesive	Spread (lb./100 sq. ft.)
Vitrite 'C' low viscosity grade	5
Catacol 688P	4
Certus (casein)	4
Aerolite 300 300F 303	3
Animal	Medium spread

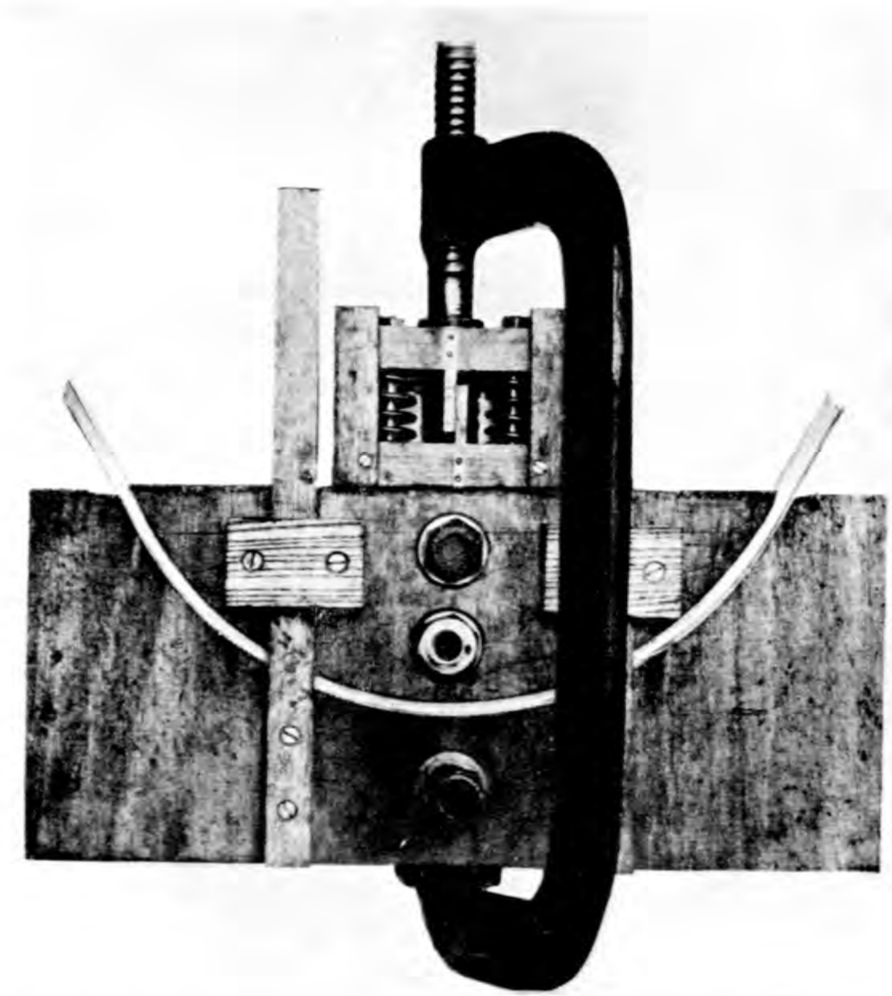


FIG. 1. SPRING-LOADED CRAMP FOR FORMING AND HOLDING BENDS TO SHAPE

III. Experimental Procedure

(a) Material Used

The material used throughout was aircraft quality Sitka spruce in the form of quarter-sawn laminae 2 ft. long by 1 in. wide and 0.06 in. thick.

Sufficient laminae were prepared so that 6 bends, each comprising 5 laminae, could be made for each particular test shown in Table 2.

After conversion, and before applying the adhesive, all laminae were conditioned to a constant weight in an atmosphere of 78° F. and 60% relative humidity corresponding approximately to 12% moisture content.

(b) Method of Making and Setting Laminated Bends

The method employed for making any bend was to glue and assemble the 5 laminae together and to press these to shape as one piece between male and female jigs (Fig. 1).

A standard type bend of 8 in. radius of curvature and embracing an angle of 120° was so produced.

A spring-loaded cramp, also illustrated in Fig. 1, was used for forcing and holding the bends initially to shape, and by this means the total pressure applied could be standardized throughout the tests.

Each bend was held in the jigs at the workroom temperature of about 70° F. for the period recommended by the glue manufacturer for the particular adhesive. As soon as the bends were released they were taken to condition in an atmosphere of 60% humidity and 78° F. temperature. These conditions were assumed to be similar to those in which bends might normally be assembled in manufacture. The diameter of each bend was determined geometrically after it had been finally stabilized at approximately 12% moisture content, and any change in diameter caused by tight clamping in the jigs was noted.

IV. Results

The results are given in Table 3 where a positive sign denotes an increase in diameter and a negative sign a decrease.

For reference purposes, each test is given the same reference number as in Table 2.

A study of the results given in Table 3 in conjunction with information given in Table 2 indicates that the final shape of a bend varied according to the type of glue used and to the method of application. Considering first the type of glue used, it can be seen that with one or two exceptions, notably bends bonded with the phenolic resins, the diameter of the bends after conditioning was smaller than the diameter of the jig.

The highest average outward movement was 0.36 in. obtained with the phenolic resin Cellobond 2661 (see Table 3, Ref. No. 47) and the highest average inward movement was 0.56 in. obtained when either animal or casein glues were used.

Of 41 tests in which a urea resin type of glue was employed, only in 8 tests was an average positive movement or increase in the diameter of the bends recorded after conditioning.

Considering next the effect of method of application of the various adhesives on the final shape of the bends, it can be seen that the diameter of all bends was smaller finally, irrespective of type of glue, when a double-sided spread as compared with a single spread was used, or when the proportion of water in the glue mix was increased. A good example is afforded in the case of Aerolite 303 and

Hardener G.M.10 single and double-sided spread (see Tables 2 and 3, Ref. Nos. 14 and 15). Bends made up with the double spread of this glue were on the average approximately $\frac{3}{8}$″ smaller in diameter finally than similar bends made up with a single spread of glue.

An example illustrating the effect of adding water to the glue mix is afforded by comparing the change in shape of bends bonded with Mouldrite Syrup 232 and Hardener G.F.2 with similar bends made with the same glue, but to which 24 parts by weight of water had been added. (See Tables 2 and 3, Ref. Nos. 32 and 36.) It can be seen that there was a difference in diameter of nearly $\frac{1}{2}$ in. between one set of bends and the next.

Finally it should be noted that the type of hardener used also had an effect on the shape of a bend. In the case of the Aerolite resins 300 and 300F, for example, a greater inward movement of the ends of the bends occurred when Hardener G.B.M. (slow setting type) was used than when the medium and fast hardeners G.B.P. and G.B.Q. were used (see Tables 2 and 3, Ref. Nos. 6, 7 and 8).

V. Discussion of Results

The results of this series of tests tend to confirm the findings of a previous investigation, where it was shown that factors influencing the moisture content of the wood, such as, for instance, the proportion of water in the adhesive, single or double spread, the quantity and the type of glue used, etc., influenced also the subsequent shape of the bend after the setting of the glue.

The change in shape that occurs is attributable to the fact that loss in moisture during conditioning causes the distance between the inner and outer surfaces of a bend to decrease without at the same time causing any appreciable change in the lengths of the bent surfaces. It is reasonable to assume that initially plane cross-sections remain plane throughout, in which case an alteration in diameter may be anticipated in order that the piece as a whole should conform to the dimensional changes that have occurred.

The movements which are likely to occur as a result of alterations in the moisture content of a bend are dealt with in the Appendix.

Apart from the effect of loss in moisture on the shape of a bend, it should be noted that any piece of timber that is bent has an inherent tendency to return to its original shape. It follows therefore that a laminated bend which has become "set" without any moisture change will, on the removal of the externally applied forces, tend to increase in diameter, i.e. the ends of the piece will tend to move outwards. The amount that the bend moves will depend on several factors such as the ratio of the thickness of the piece to the radius of curvature to which it has been bent, species, initial moisture content, etc. When several pieces are glued together in a bent shape, as in the case of a laminated bend, and the set bend is then removed from the jig, outward movement will continue until the moment of resistance induced within the piece becomes equal to the residual moments, and equilibrium is established.

It follows therefore that even if no moisture change occurs as a result of applying the glue and setting on the jig, a certain positive movement or opening out of the bend must be expected on removal of the externally applied forces. A reasonably accurate estimate of the extent of this movement could be made, but when in addition allowance has to be made for inward movements produced as a result of moisture change, the problem of arriving at the most suitable diameter of jig for producing bends of given diameter becomes much more involved.

For such reasons it has been considered in these tests that glues which in themselves, in setting and drying out cause least inward movement, are from the point of view of accuracy of shape, more suitable for bent work.

TABLE 2. DETAILS OF GLUES AND BONDING PROCEDURE

Ref. No.	Adhesive		Hardener	Mixed or separate application	Mix - parts by weight	Approx. open assembly time (Mins.)		Single or double-sided spread
						Resin	Hardener	
1	Beetle Cement	W	Blue	Separate	—	10	—	—
2			,,	Mixed	100 resin 10 hardener	—	—	Single
3		H	Red	Separate	—	10	—	—
4			Blue	,,	—	10	—	—
5			,,	Mixed	100 powder 70 water 10 hardener	—	—	Single
6	Aerolite	300	GBM	Separate	—	30	—	—
7			GBP	,,	—	30	—	—
8			GBQ	,,	—	30	—	—
9		300 F	GBM	,,	—	15	—	—
10			GBP	,,	—	15	—	—
11			GBQ	,,	—	15	—	—
12		303	GM.30	Mixed	16 resin 1 hardener	5–10	—	Single
13			,,	,,	,,	,,	—	Double
14			GM.10	,,	,,	,,	—	Single
15			,,	,,	,,	,,	—	Double
16			GM.45	,,	,,	,,	—	Single
17			,,	,,	,,	,,	—	Double
18	Beetle Cement	A	V.15	Mixed	16 resin 1 hardener	5–10	—	Double
19			,,	Separate	—	5	24 hours	—
20			,,	,,	—	5	—	—
21			GP.30	Mixed	16 resin 1 hardener	5–10	—	Double
22			B.50	,,	,,	,,	—	,,
23		AF	V.15	Mixed	16 resin 1 hardener	5–10	—	Double
24			,,	Separate	—	5	24 hours	—
25			,,	,,	—	5	—	—
26			GP.30	Mixed	16 resin 1 hardener	5–10	—	Double
27			B.50	,,	,,	,,	—	,,

TABLE 2 (contd.)

Ref. No.	Adhesive		Hardener	Mixed or separate application	Mix - parts by weight	Approx. open assembly time (Mins.) Resin	Approx. open assembly time (Mins.) Hardener	Single or double-sided spread
28	Mouldrite Syrup 232		GF 1	Mixed	80 syrup 30 hardener	Closed assembly	—	Double
29			,,	,,	,,		—	Single
30			,,	,,	80 syrup 30 hardener 10 water		—	Double
31			,,	,,	,,		—	Single
32			GF 2	,,	80 syrup 30 hardener		—	Double
33			,,	,,	,,		—	Single
34			,,	,,	80 syrup 30 hardener 8 water		—	Double
35			,,	,,	,,		—	Single
36			,,	,,	80 syrup 30 hardener 24 water		—	Double
37			,,	,,	,,		—	Single
38	Plaskon Type 250–2		Ready mixed with powdered glue	Mixed	100 powder 65 water	Closed assembly	—	Single
39				,,	,,		—	Double
40				,,	100 powder 55 water		—	Single
41				,,	,,		—	Double
42	Vitrite C	Low Vis-cosity	CH 818	Mixed	16 resin 1 hardener	5–10	—	Double
43		High Vis-cosity	CH 818	,,	,,	,,	—	Double
44			CH 648	,,	,,	,,	—	Double
45	Catacol 688P		39 P	Mixed	100 resin 14 accelerator	—	—	Double
46			,,	,,	,,	—	—	Single
47	Cellobond Rockite Resin 2661		RM 100	Mixed	100 resin 6 hardener	—	—	Double
48	Casein (Certus aircraft quality)		—	Mixed	1 powder 1.56 water	—	—	Double
49	Animal glue (Pearl form)		—	Mixed	2 water 1 glue (applied hot)	—	—	Single

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TABLE 3. THE EFFECT OF TYPE OF ADHESIVE ON THE FINAL SHAPE OF LAMINATED BENDS

Ref. No.	Type	Adhesive		Moisture content % After application of adhesive	Moisture content % After final conditioning	Change in diameter after setting and conditioning (inches) Average	Change in diameter after setting and conditioning (inches) Range
1	Non-gap UF	Beetle Cement	W	29.6	12.2	—0.02	+0.12 to —0.10
2				29.7	12.8	+0.06	+0.14 to —0.14
3			H	35.3	12.6	—0.32	—0.42 to —0.22
4				28.0	12.0	—0.16	—0.28 to —0.08
5				29.0	12.5	—0.14	+0.10 to —0.42
6	Gap-filling UF	Aerolite	300	24.7	12.0	—0.28	—0.34 to —0.16
7				25.8	11.6	—0.04	+0.12 to —0.30
8				31.0	12.2	—0.06	+0.06 to —0.26
9			300F	30.5	12.7	—0.52	—0.68 to —0.38
10				23.1	12.6	—0.10	—0.18 to 0
11				22.8	12.0	—0.24	—0.30 to —0.20
12			303	21.4	11.2	—0.08	+0.10 to —0.22
13				26.1	12.6	—0.16	—0.30 to —0.10
14				22.9	12.3	—0.02	+0.14 to —0.14
15				27.8	12.3	—0.40	—0.42 to —0.36
16				18.7	12.2	+0.12	+0.28 to —0.02
17				23.2	12.3	—0.14	—0.22 to 0
18		Beetle Cement	A	33.6	11.5	—0.22	—0.42 to 0
19				23.6	11.4	—0.02	+0.24 to —0.22
20				26.0	11.2	0	+0.14 to —0.32
21				31.8	11.7	—0.37	—0.66 to —0.18
22				24.6	10.6	—0.26	—0.64 to —0.02
23			AF	33.4	10.7	—0.26	—0.42 to +0.12
24				24.6	11.9	—0.10	+0.34 to —0.32
25				35.5	11.6	—0.36	—0.60 to 0
26				31.0	10.7	—0.20	—0.42 to 0
27				30.7	10.6	+0.06	+0.18 to —0.02

TABLE 3 (contd.)

Ref. No.	Type	Adhesive	Moisture content %		Change in diameter after setting and conditioning (inches)	
			After application of adhesive	After final conditioning	Average	Range
28	Gap-filling UF	Mouldrite Syrup 232	29.5	11.2	—0.04	+0.12 to —0.06
29			23.4	12.3	+0.04	+0.10 to —0.02
30			29.1	11.2	—0.34	—0.24 to —0.42
31			24.6	12.8	—0.06	+0.14 to —0.16
32			24.3	11.6	0	+0.14 to —0.06
33			20.4	11.8	+0.16	+0.26 to +0.04
34			29.8	12.1	—0.24	—0.30 to —0.18
35			—	12.3	0	+0.08 to —0.08
36			37.2	12.2	—0.42	—0.52 to —0.32
37			—	11.9	—0.22	—0.32 to —0.16
38		Plaskon Type 250–2	23.7	10.7	+0.12	+0.28 to +0.02
39			28.9	12.0	—0.12	—0.24 to —0.08
40			27.2	12.1	+0.14	+0.26 to +0.06
41			28.4	12.1	—0.02	+0.14 to —0.16
42		Vitrite C Low Viscosity	18.2	11.3	+0.12	+0.40 to —0.08
43		Vitrite C High Viscosity	23.6	11.8	—0.24	—0.38 to —0.06
44			24.5	12.0	—0.20	—0.36 to —0.06
45	PF	Catacol 688P	24.4	10.2	+0.26	+0.38 to +0.12
46			20.5	11.8	+0.30	+0.60 to —0.08
47		Cellobond 2661	14.6	11.6	+0.36	+0.42 to +0.28
48	Casein	Certus (aircraft quality)	39.9	11.6	—0.56	—0.66 to —0.52
49	Animal glue	Pearl form	44.5	12.8	—0.56	—0.64 to —0.42

It may be argued that it should be possible by using drier laminae and a controlled glue spread to prevent any change in moisture content of the bend during the conditioning treatment and hence change of shape, irrespective of type of glue used. This would, however, have a detrimental effect on the bending properties of the laminae.

On the base of comparison outlined above, the types of glues included in this investigation may be placed in the following order of merit for use in laminated bentwork when accuracy of shape is of prime consideration :

Phenolic resin
Urea-formaldehyde
Casein
Animal

It must be stressed that no reference whatever has been made in these tests to the strength, moisture-resisting or other properties of the glues, which naturally need to be considered before a proper selection can be made for any particular job.

VI. Conclusions

The results obtained confirm that any factor in the gluing process, such as type of glue, method of application, etc., which affects the moisture content of the laminae also affects the subsequent shape of the bend after the setting of the glue.

Providing other properties of the laminated part such as strength of the glued joints are not impaired, the amount of glue spread should always be kept at a minimum in order to reduce subsequent movement.

Furthermore, should the glue be extended by the addition of water, the effect on the final shape of the bends should not be overlooked.

A comparison of the different types of glues used in these tests would indicate that the synthetic resins, particularly of the phenol-formaldehyde variety, tend generally to produce rather more satisfactory results than casein or animal glues in manufacturing laminated bends where accuracy of shape is an essential feature.

It cannot be said, however, that the use of even a synthetic glue will entirely inhibit all subsequent movement.

VII. Appendix

Theoretical Considerations of the Movement of Bends Consequent upon Changes in Moisture Content

Loss of moisture in a piece of bent wood will cause both its width and thickness to diminish but will not materially affect the longitudinal dimensions unless considerable compression has occurred in this direction. In laminated bends, longitudinal compressive strains are generally comparatively small and each lamination behaves, as far as dimensional changes due to moisture are concerned, in much the same way as in the unbent state. When drying takes place in a laminated bend that is "set", there is a tendency for the inner and outer surfaces to come closer together without any appreciable change occurring in the lengths of these surfaces. It is reasonable to suppose, and tests have borne out, that initially plane cross-sections of the piece tend to remain plane, in which case it becomes necessary for the radius of curvature of the bend to alter in order that the piece as a whole should conform to the dimensional changes that have occurred.

Suppose the original thickness of a bend made to a form radius "r" to be "t" and that this shrinks by an amount "e" per unit of thickness so that the final thickness of bend is $t(1-e)$. The lengths l_1 and l_2 of the inner and outer surfaces respectively remain virtually unchanged so that if the assumption that plane sections remain plane is valid, then the following relations hold :

namely $\frac{l_1}{r'} = \frac{l_2}{r'+t\,(1-e)}$ where r′ is the new radius of curvature.

But $\frac{l_1}{r} = \frac{l_2}{r+t}$

so that $\frac{r}{r'\,(r+t)} = \frac{1}{r'+t\,(1-e)}$.

Hence $r\,r' + rt\,(1-e) = r\,r' + r'\,t$ or $r' = r\,(1-e)$.

This result is of interest as it indicates that the percentage decrease in radius of curvature should be exactly equal to the percentage decrease in the thickness of the bend caused by moisture loss.

Similarly it can be shown that the unit increase in the angle of bend expressed in radians should be equal to $\frac{e}{1-e}$.

Report No. 5

The Part Played by Formaldehyde in Dermatitis Attributable to Synthetic Resin Glues

(Based on Ministry of Aircraft Production Scientific and Technical Memorandum No. 21/45, November, 1945)
by G. E. Little, Department of Scientific and Industrial Research

U.D.C. No. 668.3 : 679.56

Abstract

The free formaldehyde content of a series of phenol-, urea- and resorcinol-formaldehyde glues, alone and mixed with hardener, has been determined. The formaldehyde content of the urea and phenolic glues was between ¼ and 5½%. There was no distinction on the basis of formaldehyde content between the two types of resin and in only one sample was there any evidence for a marked increase in the formaldehyde content on addition of hardener. The resorcinol resins contained no free formaldehyde; but after treatment with hardener the amount of free formaldehyde increased slowly, attaining a value of 2½% in 2 hours at 25° C. The concentration of formaldehyde vapour in the air in proximity to the glues was also estimated. The values obtained were a function only of the formaldehyde content of the glue, irrespective of its chemical nature. A similar result was obtained for resin-hardener mixes excepting those which liberated considerable heat during setting.

The results summarised above have been correlated with data on the incidence of dermatitis among operatives working with these glues. It is concluded that:

(a) outbreaks of dermatitis affecting about 5% of the operatives may be attributed to formaldehyde vapour,

(b) where half or more of the operatives are affected by dermatitis the primary cause is hardening of the glue on the skin.

High standards of cleanliness and the use of barrier creams appear to be the most effective means of avoiding dermatitis. The development of water-soluble, low formaldehyde content glues would tend to reduce the incidence of dermatitis.

Contents

Illustrations

I. Introduction

The superiority of synthetic resin adhesives over other cold setting glues has led to their widespread use, particularly in the aircraft industry. Their introduction has, however, been attended by new problems, possibly the most serious being the development of dermatitis by those who handle the glues. The incidence of the trouble has been so high in certain cases as to necessitate the use of a glue of lower durability. It has been asserted that certain phenolic glues, which from laboratory tests might be expected to give the highest performance in service, are more troublesome than the urea based adhesives. In order, therefore, to facilitate the choice of adhesives it is desirable to reduce the incidence of dermatitis.

In order to obtain data on the incidence and causes of the affection, a number of firms were approached. It was generally agreed that dermatitis can arise through :

(a) The hardening of the glue on the skin,
(b) The action of the vapour of formaldehyde,

but as to which was the primary cause, there was a divergence of opinion.

Accordingly experiments have been carried out in order to correlate the proportions of formaldehyde in a glue and the surrounding air with its dermatitic properties in order to deduce, if possible, which of the two causes of dermatitis is paramount.

II. Determination of the Formaldehyde Content of Selected Synthetic Resin Glues

(a) Gravimetric Method

Dimedone (dihydrodimethyl resorcinol) reacts quantitatively with formaldehyde to yield methylene bis-dihydrodimethyl resorcinol.[1] This reaction was used in the determination of the formaldehyde content of certain phenolic resin and resin-hardener mixes.

In Table 1 are shown the figures for three phenolic resins, alone, or mixed with hardener. Each value is the mean obtained from two determinations.

TABLE 1. FORMALDEHYDE CONTENT OF PHENOLIC RESIN GLUES

Glue	No hardener present	Hardener present		
	% CH_2O by wt.	% CH_2O by wt.		
		Minutes after mixing		
		0	15	30
PF 1a	6½	6½	6½	7½
PF 4a	3½	3¼	3¼	3
PF 5	¾	¾	¾	¾

The method was not applicable to urea resins. These, being water soluble, could not easily be removed by precipitation. Dimedone added to a solution of the resin was completely precipitated. Evidently formaldehyde was liberated by the resin.

(b) Colorimetric Method

Schryver[2] has shown that when a solution of formaldehyde phenylhydrazone is treated with potassium ferricyanide and hydrochloric acid a deep red coloration develops. The intensity of the colour can be used to determine the amount of formaldehyde either by comparison with a set of standards, or alternatively by means of a photoelectric cell. The test is sensitive and can be used for the estimation of the amount of formaldehyde in the air; it was for this purpose that it was primarily used in this work. But in addition, it was applied to the determination of the formaldehyde content of the resins themselves. The experimental technique is fully described in Section VI; in this place results only will be considered.

In Table 2 are shown the results of determinations of the formaldehyde content of five phenolic, two urea and two resorcinol resins, all well known commercial resins except the resorcinol resin RF 2, which was prepared at C.R.L. The results of individual determinations have been given, rather than mean values, in order to give some idea of the reproducibility of the method. In certain cases two batches of the same resin, obtained from the manufacturer at different periods, were examined. These are designated by the suffixes "a" and "b". As with the dimedone method it was necessary to precipitate the phenolic resins; but the remaining resins, being water soluble, were not so treated. In the case of the urea resins, it is possible that errors may have been introduced due to (a) the effect of dilution, (b) the presence of acid during part of the test. The former would lead to low values, the latter to high values.

TABLE 2. FORMALDEHYDE CONTENT OF SELECTED RESIN AND RESIN-HARDENER MIXES

Glue	No hardener present	Hardener present										
	% Formaldehyde	% Formaldehyde										
		Minutes after mixing										
		0	10	15	20	30	35	40	45	60	120	150
PF 1a	5½, 5¾											
b	5½, 5½, 5, 5¾			5		7			8½			
UF 1	4, 4, 3¼		3½		3¼			2½				
PF 2a	4, 3, 4, 3½, 3½			3½			3¼			3¾		
b	2½, 3			3¼					3¼			
PF 3a	3¾			4		3¾			3¾			
b	3¾, 4											
UF 2a	1½, 1½, 1¾, 1¾			1½		1½		2				
b	2, 2											
PF 4a	3, 3½, 3	3½		3½		3½						
b	2¼, 2¼			2¾		2			2¾			
RF 1	Nil	½		¾		1			1¼		2½	3
RF 2	Nil	¾		¾		1			1¼		2½	
PF 5	½, ½, ¼, ¼			¼		¼			¼			

The following conclusions may be drawn from the results listed in Tables 1 and 2:

(1) There is fairly good agreement between the methods. A time lapse of some weeks occurred between the two sets of determinations; this would be accompanied by changes in the glues.

(2) Different batches of glue obtained from manufacturers generally show good agreement; PF 4 appears to be an exception.

(3) The resorcinol resins were themselves free from formaldehyde; when treated with a paraform hardener, the formaldehyde content increased with time.

III. Determination of the Concentration of Formaldehyde in the Air in Proximity to the Glue

(a) Details of Apparatus

The apparatus is shown diagrammatically in Fig. 3. It consisted of a container for the glue, a desiccator maintained at 25° C., and a device for withdrawing samples of air from it in order to determine their formaldehyde content. It was possible to stir either the glue or the air above it, but not both. A full description of the apparatus is given in Section VI.

TABLE 3. APPROXIMATE CONCENTRATION OF FORMALDEHYDE IN AIR IN PROXIMITY TO THE RESIN

Resin	% Formaldehyde in resin	Concentration of formaldehyde, mg./litre Volume air withdrawn	
		230 c.c.	380 c.c.
PF 1b	5½	10×10^{-2}	16×10^{-2}
UF 1	4	4×10^{-2}	10×10^{-2}
PF 2a	3½	4×10^{-2}	8×10^{-2}
PF 3a	3¾	4×10^{-2}	5×10^{-2}
PF 4a	3½	3×10^{-2}	5×10^{-2}
UF 2a	2	2×10^{-2}	4×10^{-2}
PF 5a	½	1.5×10^{-2}	2×10^{-2}

(b) Experiments in which the Glue was Stirred

(1) *No hardener present.* A sample of resin, approximately ½ lb. in weight, was contained in the desiccator. The glue was stirred for 1¼-1½ hours at, as far as possible, 70-90 r.p.m. Samples of the air in the desiccator were then withdrawn and analysed, stirring continuing. The time required for sampling was about one hour.

Distribution of formaldehyde in the desiccator was far from uniform, earlier samples were devoid of the gas, later samples considerably enriched; moreover successive samples showed a scatter. In Table 3 are given values for the mean concentration in mg./litre for the first 230 and 380 c.c. withdrawn. They are the mean of a number of determinations.

The main fact illustrated by these figures is that the formaldehyde concentration in the air is a function of that in the glue. The maximum concentration, allowed by the American Standards Association for factories, etc., is 1.2×10^{-2} mg./litre.

(2) *In the presence of hardener.* A urea or phenolic resin could not be mixed with hardener, placed in the desiccator, and stirred for 1¼-1½ hours since gelling occurred. Accordingly, in order to obtain some information as to the formaldehyde content of the air associated with the glue-hardener mixes, untreated resin was stirred for 1¼-1½ hours, hardener was added, and after mixing, sampling commenced. The resorcinol resins on the other hand, having a longer pot life could be treated with hardener, stirred for 1¼-1½ hours, and then sampled. In all cases, however, difficulties due to gelling affected the uniformity of stirring. In Table 4 the mean formaldehyde concentration of the first 230 c.c. withdrawn is listed for a number of the glues.

TABLE 4. APPROXIMATE CONCENTRATION OF FORMALDEHYDE IN THE AIR ABOVE GLUE-HARDENER MIXES

Resin	% of Formaldehyde in resin	Average Concentration of Formaldehyde, mg./litre
RF 1	up to 3	3×10^{-2}
RF 2	up to 3	2×10^{-2}
PF 2a	3½	4×10^{-2}
PF 3a	3¾	4×10^{-2}
PF 4a	3¾	5×10^{-2}
UF 2a	2	2×10^{-2}
PF 5	½	5×10^{-2}

In comparison with the figures in Table 3, the most striking change is associated with PF 5. This resin heated very considerably after addition of hardener. In general, however, no very marked changes occurred on addition of hardener.

(c) Air Above the Resin Agitated

In order to afford a better comparison between the resin and resin-hardener mixes, the air above the glue was stirred, and not the glue. Samples of resin were placed in the desiccator, and the air above these was agitated for 1½ hours before sampling commenced, in order to allow the attainment of equilibrium. The experiment was repeated, using a glue-hardener mix. As the whole experiment took 2½ hours, the phenolic and urea glues had set before the final samples were withdrawn.

Finally glue-hardener mixes were placed in the desiccator and the air above them was stirred for ½ hour, when sampling was commenced. The method of sampling used in this experiment was as follows: 10 samples of 50 c.c. were withdrawn, and the first four discarded. The mean formaldehyde content of the remaining six was determined, the blank experiment being carried out with water instead of glue contained in the desiccator.

Four glues RF 1, UF 2b, PF 2b, and PF 3b were examined. The results are shown in Table 5.

TABLE 5. APPROXIMATE CONCENTRATION OF FORMALDEHYDE ABOVE SELECTED RESIN GLUES

Glue	% of Formaldehyde in glue	Concentration of Formaldehyde, mg./litre		
		No hardener	Hardener	Hardener
		1½ hr. stirring	1½ hr. stirring	½ hr. stirring
RF 1	0—3	——	1×10^{-2}	3×10^{-2}
UF 2b	2	3×10^{-2}	3×10^{-2}	1×10^{-2}
PF 2b	3½	5×10^{-2}	2×10^{-2}	3×10^{-2}
PF 3b	3¾	5×10^{-2}	3×10^{-2}	2×10^{-2}

The most important conclusion to be derived from Tables 3 and 5 is that the urea resin UF 2 does not differ greatly from PF 3 and PF 2. The significance of this will be discussed below. It will be further noted that stirring the glue gives rise to a higher concentration of formaldehyde than stirring the air.

IV. Conclusions Derived from the Work Described in II and III

(1) The formaldehyde content of the resins varied from 0% in the case of the RF resins to 5½ and 6% in that of PF 1. There was no distinction between the urea and phenolic resins with respect to formaldehyde content.

(2) The formaldehyde content of the air in proximity to the glue is related to the formaldehyde content of the resin and does not depend on whether this is of the urea or phenolic types.

(3) No evidence was obtained from the experiments on urea and phenolic resins that any marked evolution of formaldehyde occurs on mixing with hardener. In certain cases a small increase in the formaldehyde content of the glue occurs; in others a slight increase in the formaldehyde content of the air in proximity to the glue. Heating of the resin during setting also gives rise to higher formaldehyde concentrations in the air. The resorcinol resins when treated with hardener are associated with increasing concentrations of formaldehyde, both in the glue and in the surrounding air.

V. Correlation of Formaldehyde Content with Incidence of Dermatitis

A certain amount of data was available as to the incidence of dermatitis arising from the use of a number of the glues examined. The evidence was, however, somewhat scanty, and any conclusions outlined below might be vitiated if further data were available.

The three probable causes of the affection are:

(1) The action of formaldehyde vapour.

(2) The hardening of the glue on the skin followed by,

  (a) the irritant action of formaldehyde, phenol, or phenolic alcohols,

  (b) the forcible removal of layers of glue with damage to the skin and consequent vulnerability to infection.

(3) The use of organic solvents as cleansing agents.

Although organic solvents have dermatitic properties, their use as cleansing agents is restricted and they cannot be considered as the primary cause of the affection.

A small number of people are potentially allergic to formaldehyde vapour, and even though they do not handle glues they will be affected. From evidence available it would appear that the number of such persons should not exceed 5 per 100. When, as has been asserted, an outbreak of dermatitis affects half or even more of the workers there is reason for believing that the primary cause is the hardening of the glue on the skin and not formaldehyde in the atmosphere. The evidence adduced for this hypothesis is as follows:

(1) Hot-press glues are usually associated with high concentrations of formaldehyde vapour, yet they are seldom troublesome. Glues used in this operation are slow setting and in general more water soluble than the cold setting variety. Consequently the probability of hardening of the glue on the skin is small.

(2) Although no complaints have been received against UF 1 used cold, much trouble has been experienced with PF 2 and PF 3 which are associated with lower formaldehyde vapour concentrations. A firm, forced to abandon these latter glues

owing to widespread dermatitis, successfully substituted UF 2, the formaldehyde vapour concentration of which is not much smaller than that of PF 2 and PF 3.

These phenomena may best be explained by the fact that whereas urea glues are water soluble and retain that property for some time after mixing with hardener, the phenolic glues are at the outset 50% insoluble in water; consequently retention of phenolic glue on the skin is almost certain, whereas that of the urea resins can be largely avoided.

(3) One firm using UF 2 reported little dermatitis, another was forced to abandon its use. Only lack of cleanliness can be responsible in this case, hardening of the glue on the skin causing the affection. Significantly formaldehyde was in use at this firm in other operations; the vapour concentration was high, yet no cases of dermatitis occurred.

(4) A firm engaged on the manufacture of urea-formaldehyde and phenol-formaldehyde resins reported freedom of dermatitis in the case of the former, and a small incidence which was attributed to phenols, in the latter.

(5) Outbreaks of dermatitis have been overcome by the application of methods designed to prevent hardening of the glue on the skin, particularly by the use of barrier creams.

VI. Experimental Details

(a) Gravimetric Determination of Formaldehyde

0.2-0.5 gm. resin or resin-hardener mix was dissolved in about 10 c.c. alcohol. The solution was added to a mixture of 50 c.c. water, 1 gm. sodium chloride, and a few drops of acetic acid. The resin was precipitated by shaking for one hour and was removed by filtration through a sintered glass crucible. To the filtrate were added a few drops of acetic acid and the appropriate amount of a 10% alcoholic solution of dimedone. After 48 hours the precipitated methylene bis-dihydroresorcinol was isolated by filtration, dried and weighed.

(b) Photoelectric Cell

(1) *Theory.* If a beam of light is allowed to impinge on a photoelectric cell connected to an ammeter, then a current will be recorded, varying with the intensity of the light. If now a coloured solution be placed between the source of light and the cell, there will be a reduction in the observed current. When a number of Schryver's Test Solutions were examined it was found that the amount of reacted formaldehyde, C_f, varied inversely with the observed current, i, provided the solutions were very dilute. This is expressed in equation (1):

$$C_f = K/i + k \qquad \ldots (1)$$

where K, k are constants.

(2) *Experimental details.* The photoelectric cell was set up as indicated in Figs. 1a, b. A mounted cell, A, having a circular aperture 1″ in diameter was encased in a wooden frame B, and was covered by a wooden pyramid C. This contained a cylindrical aperture of diameter 1.1″ which fitted over the cell aperture. The cell was connected to a microammeter.

The source of light was a car headlamp, arranged above the cell and operated by six accumulators, "floating" on the mains. Direct mains supply was too variable to allow of its use. The filament temperature was controlled by the sliding wire resistance R_1 and the mains output by the rheostat R_2. An ammeter was included in the circuit to check the input and output currents. In order to restrict as far as possible changes in the character of the light emitted by the

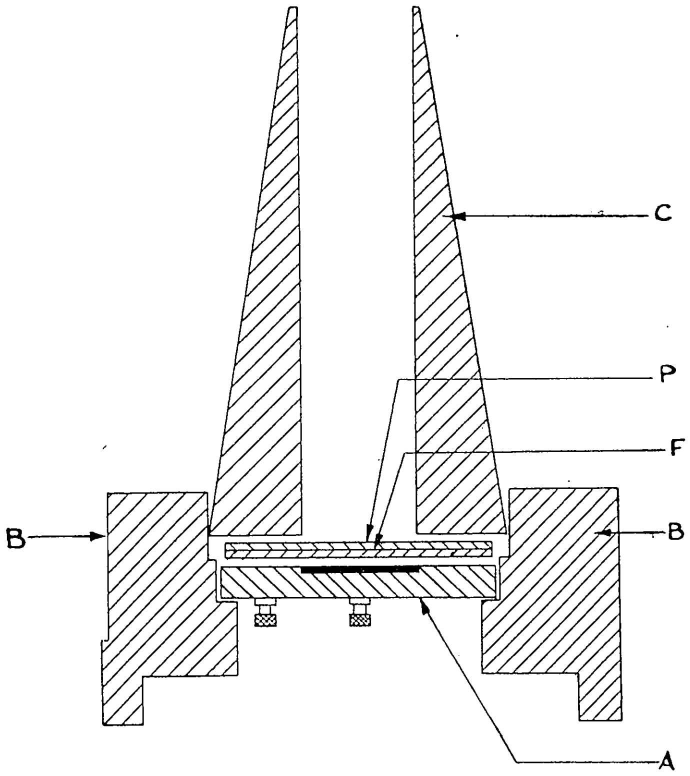

Fig. 1 (a). PHOTOELECTRIC CELL

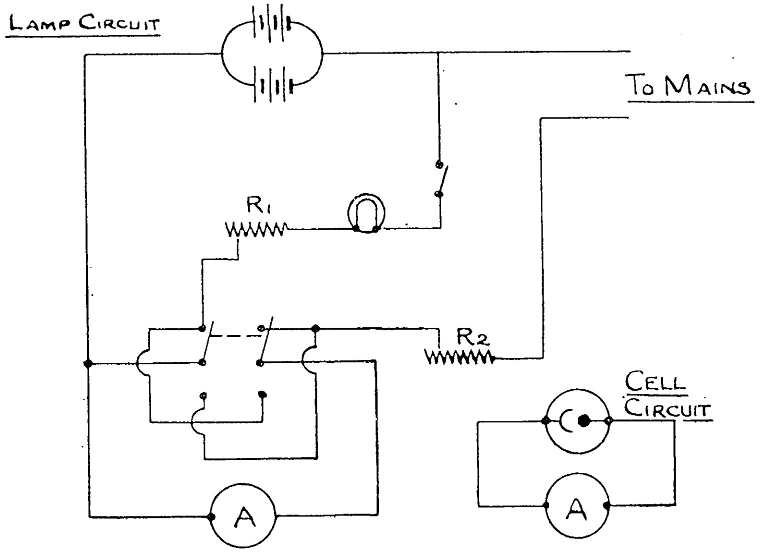

Fig. 1 (b). ELECTRICAL CIRCUIT

filament, a blue green filter F, protected by a cover glass P was placed above the cell. A further plate was placed below the headlamp to restrict the heating of the cell and its contents. In daylight unless the headlamp was on, no scale reading was recorded by the microammeter, implying that the cell was well blacked out.

The solution to be examined was placed in a cylindrical silica glass tube, 1″ in diameter and 4½″ long, having an optically flat base. A similar tube contained 20 c.c. of distilled water and served as a standard. In order to take a reading the standard was placed in the pyramid and by varying R_1 the microammeter deflection was adjusted to 85, an arbitrary figure. The reading observed on substituting the other tube was recorded.

(c) Standardisation of the Cell

(1) A 5% formaldehyde solution was prepared by diluting commercial formalin, taken to be 40%. Experiment later showed that the true value was 38%. The accuracy of the experiments was such, however, that the application of this correction might be waived.

Solutions A and B were prepared by diluting 0.51 gm. of the 5% formaldehyde solution to 200 c.c.; 20 c.c. of this solution were diluted to 1 litre. A and B should have contained the same amount of formaldehyde.

The mixtures listed in Table 6 were then made up.

TABLE 6

Solution	a	b	c	d	e	f
Water	13	11½	10	8½	7	5½
1% Phenylhydrazine hydrochloride	2.0	2.0	2.0	2.0	2.0	2.0
Solution A (B)	0	1½	3	4½	6	7½

The reaction between the formaldehyde in solutions A (B) and the phenylhydrazine hydrochloride was given 3 minutes. Each solution was then treated with 0.8 c.c. 5% potassium ferricyanide solution and immediately after with 4 c.c. concentrated hydrochloric acid; after 15-20 minutes it was examined photoelectrically.

In Table 7 are shown the figures obtained from the photoelectric cell for solutions a-f for each of A and B. They give an idea of the reproducibility of the method.

TABLE 7. EXAMINATIONS OF SOLUTIONS BY THE PHOTOELECTRIC CELL

Volume of Solution A (B)	Solution A		Solution B	
	Ammeter Defln. S	λ = 100/S	Ammeter Defln. S	λ = 100/S
0	52½	1.9	—	—
1½	38½	2.6	38½	2.6
3	26	3.8	27	3.7
4½	22	4.5	19½	5.1
6	18	5.6	16½	6.1
7½	14½	6.9	12½	8.0

If the reciprocal of the current is proportional to the quantity of the formaldehyde solution, on plotting λ (100/Ammeter Reading) against number of c.c. of solution A or B, a straight line should be obtained. In Fig. 2a, the meaned values of λ_A and λ_B are plotted against number of c.c. of solution taken. Linearity is obeyed for values of $\lambda < 6$. By determining the gradient of the graph, the cell constant could be calculated. For convenience, however, another form of

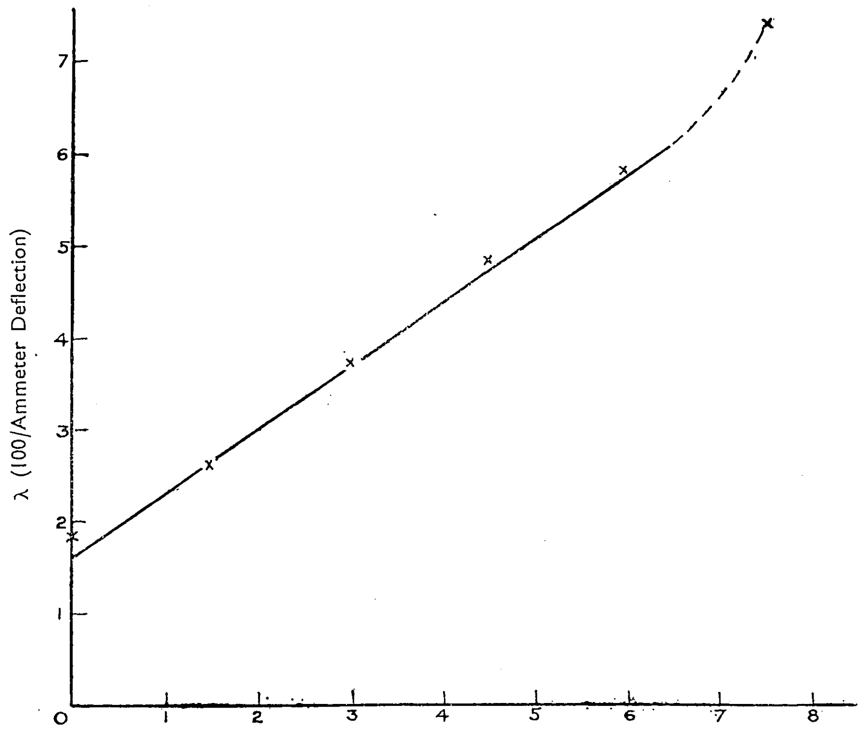

FIG. 2a. CALIBRATION OF PHOTOELECTRIC CELL. METHOD FOR DETERMINATION OF FORMALDEHYDE

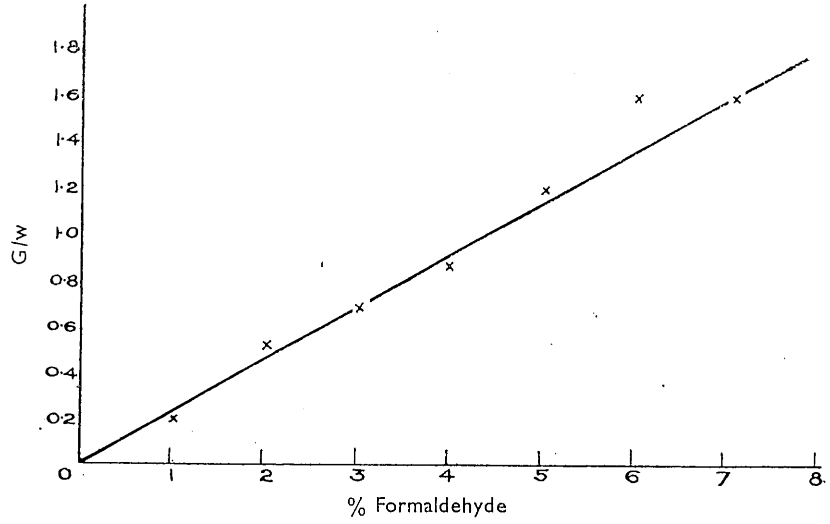

Fig. 2b. STANDARD CURVE FOR DETERMINING % OF FORMALDEHYDE IN A GLUE

equation (1) relating directly the percentage of formaldehyde in the original solution, p, the weight of solution taken, w, and the gradient of the graph G, was used. This was as follows:

$$p = K_p \cdot \frac{G}{w}. \qquad \ldots (2)$$

This graphical method of interpreting the results was preferred to the determination of the mean amount of formaldehyde in a number of samples of say 5 c.c. since the cell had a positive zero value.

(2) Other formaldehyde solutions were prepared and suitable volumes, up to 10 c.c., were tested. In Fig. 2b the values of G/w are plotted against p, the percentage of formaldehyde in the original solution. Linearity is obeyed as would be expected from equation (2).

(d) Determination of the Formaldehyde Content of Resins and Hardener Mixes

A resin or resin-hardener mix can be regarded as a solution of formaldehyde of concentration p per cent. If a weight w were taken, diluted to 200 c.c. and 20 c.c. of the solution were diluted to 1 litre, then the value G could be determined as for the solutions described under (c). G and w being known, p, could be read off from the graph in Fig. 2b.

This method was adopted with the soluble resins, though fillers had to be removed by filtration of the 200 c.c. solution. Phenolic resins, however, being insoluble in water required special treatment. The method was as follows:

0.5 gm. was dissolved in about 5 c.c. alcohol, and added to 20 c.c. of strong salt solution, a further 5 c.c. of alcohol being used for washing. The mixture was agitated in a high-speed shaker (500 vib./min.) for about 30 minutes. The clear liquid was decanted into a 200 c.c. measuring flask, diluted to 200 c.c. and filtered, if necessary. 20 c.c. of this solution were diluted to 1 litre and examined as under (b).

(e) Description of Apparatus as shown in Fig. 3

A desiccator D was fitted with a mechanical stirrer and contained a beaker, B, in which was placed the glue to be examined. Air was withdrawn from the top of the desiccator and entered via the stirrer sleeve. In the experiment, where the glue was stirred, the bottom of the sleeve was about 1″ above the surface of the glue. When the air was stirred, however, the sleeve was cut by about 1″ in order to give more freedom to the stirrer.

The sampling apparatus consisted of a bubbler, S, in which the absorbing liquid was contained, and a small aspirator, A, to draw the gas from the desiccator. A small mercury bubbler, M, was placed between the sampler S and the desiccator to prevent abnormal absorption of formaldehyde through diffusion. The flowmeter F was included as a check against leaks. The tap T_2 was always open during sampling.

In order to withdraw a sample of gas, the tap T_1 was opened to the atmosphere, then by opening T_3 and T_4 water was allowed to flow from the aspirator. (T_4 was used as a control tap in order to adjust the rate of flow of gas through S. This was kept between the limits 10-12 c.c./min. at which speed absorption of formaldehyde was effectively complete.) When air bubbled through S, T_1 was reversed and gas allowed to pass from the desiccator until the required volume of water had collected in the cylinder C. T_1 was again reversed and 10 c.c. more water were allowed to collect in C, in order to clear the glass tube between S and T_1 of formaldehyde. T_3 was now closed, S withdrawn and its contents analysed photoelectrically.

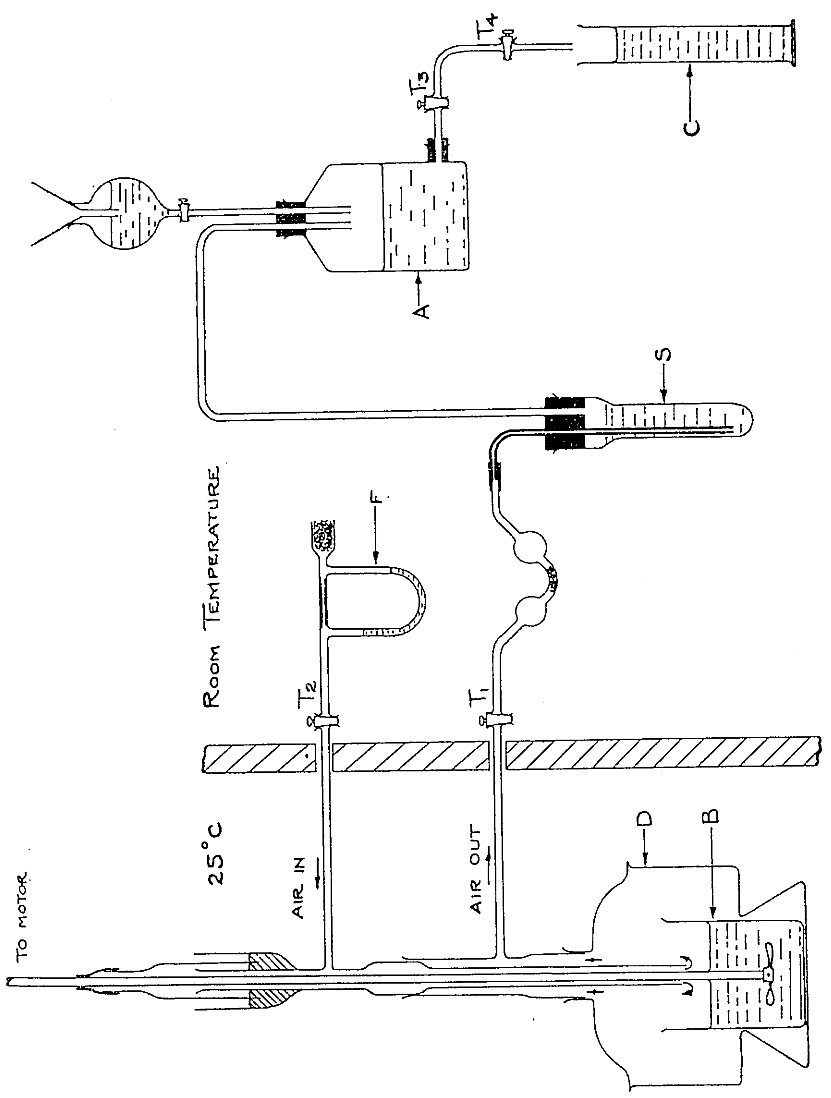

FIG. 3. APPARATUS FOR EXAMINATION OF AIR ABOVE GLUE

(f) Derivation of the Figures in Tables 3, 4 and 5

The amount of formaldehyde in a sample of gas was determined as follows:

2.0 c.c. of 1% phenylhydrazine hydrochloride solution and 6½ c.c. of water were placed in the absorber S. After the gas had passed through S, the contents were transferred to a tube and treated with a further 6½ c.c. of water (from washing out S), 0.8 c.c. 5% potassium ferricyanide and 4 c.c. concentrated hydrochloric acid. After 15 minutes the colour intensity was measured by the photoelectric cell.

If C_{f_1}, C_{f_2} were the concentration of formaldehyde in two samples of air, i_1, i_2 were the corresponding currents flowing from the cell,

then

$$C_{f_1} = K/i_1 + k$$

$$C_{f_2} = K/i_2 + k$$

$$\text{therefore } C_{f_1} - C_{f_2} = k\left(\frac{1}{i_1} - \frac{1}{i_2}\right) = K^1(\lambda_1 - \lambda_2).$$

$$\text{If} \qquad C_{f_2} = 0 \quad \lambda_2 = \lambda_0$$

$$\text{therefore } C_{f_1} = K^1(\lambda_1 - \lambda_0). \qquad \ldots (3)$$

In deriving the figures in Tables 3-5 use has been made of this equation. λ_0 was either determined from a blank experiment in which water was substituted for the glue, or from samples which were virtually free from formaldehyde. The constant K^1 is related to K_P in equation (2) and can be derived arithmetically from it.

VII. Conclusions and Recommendations

It may be concluded that:

(1) Some dermatitis will arise through allergy of particular workers to formaldehyde vapour.

(2) Serious outbreaks of dermatitis are primarily attributable to hardening of the glue on the skin.

Whilst it is true that the use of barrier creams and high standards of cleanliness will theoretically reduce the incidence of dermatitis to the few cases of allergy, it is extremely difficult to attain this objective in practice because of the human element.

Both causes of the trouble would tend to be eliminated by the development of low formaldehyde content water soluble glues.

VIII. Bibliography

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Relevant Reports

The undermentioned reports, relevant to the subject of this volume, are included in Plastics, Volume 1 of the Selected Government Research Report series.

VOLUME 1—PLASTICS.
REPORT No. 19. U.D.C. No. 668.3 : 679.56

Synthetic Resin Glues

The Influence of pH on the Rate of Hardening of Cold Setting Glues

(Based on Ministry of Aircraft Production Scientific and Technical Memorandum 2/45. 7th January, 1945)
By G. E. Little

The setting time-hardener concentration curve for the glue is determined by the strain gauge technique, and the initial pH-hardener concentration curve by means of the glass electrode. From these curves the relationship between the initial pH and setting time is deduced.

VOLUME 1—PLASTICS.
REPORT No. 20. U.D.C. No. 668.3 : 679.56

Synthetic Resin Glues

The Setting Time-pH Characteristics of Cold Setting Resins Prepared from Some Monohydric Phenols

(Based on Ministry of Aircraft Production Scientific and Technical Memorandum 15/46. April, 1946)
By G. E. Little, H. M. Paisley.

Experimental results in tabular form are given on the viscosity of resins, effect of pouring condensate into water, neutralisation of the catalyst, time of condensation nature of catalyst, and molecular ratio nature of phenol. It is concluded that the setting pH of resins based on the condensation of phenol and formaldehyde was largely independent of the method of preparation. The "failing pH" was never higher than 1.3.

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