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Studies of the factors controlling the action of hair sprays II. The adhesion of hair spray resins to hair fibres

R. W. RANCE*

Synopsis—Measurements have been made of the ADHESION of HAIR SPRAY RESINS to HAIR FIBRES and the importance of adhesion in determining hair spray properties is discussed. The similarities between the technology in the bonded fabric field and in the hair spray field are considered and useful extrapolations concerning adhesion and other resin properties may be made. For good adhesion at least two requirements are apparently necessary. The viscosity of the resin solution must be low so that the resin remains in close interfacial contact with the fibre throughout the large dimensional changes occurring as the solvent evaporates. Also the resin itself must be sufficiently deformable to allow any stresses due to these dimensional changes to be dissipated and to enable the dried joint to withstand impact and bending. These factors, which emerge from earlier studies of adhesion, are found to be applicable in the present study.

INTRODUCTION

Polymer adhesion to wool fibres is known to be an important factor in the production of anti-felting properties on wool fabrics (1), and in the manufacture of non-woven textiles (2–4). Tikhomirov and Gusev have reported an investigation of the structural bonds and the properties

* Unilever Research, Isleworth, Laboratory, 455 London Road, Isleworth, Middlesex.

of bonded fabrics, and consider that the strength of the bond between the binder and the fibre is one of the principal factors in the tensile strength of such fabrics (4). The strength of this bond depends mainly on the forces of adhesion which characterize the efficiency of the binder. These authors give results of measurements of the adhesion of polymeric binders to wool fibres and those results are among the first attempts at an experimental determination of the adhesion of polymers to natural fibres. Similar measurements on hair fibres do not seem to have been reported.

The requirements of a good adhesive have been defined (5, 6) as the ability to wet the adherend, to be solid at the temperature of usage, and to be sufficiently deformable to minimize stress concentrations during solidification. This latter requirement is also advantageous in the hairspray field since the resin bridges will be less liable to fracture during flexing of the hair fibres.

Good adhesion of a hairspray resin to hair combined with good tensile properties of the resin will promote strong and lasting hold, while poor adhesion will give poorer hold but easy elimination on brushing or combing.

The adhesive power of polymeric materials is normally assessed from tests on large specimens where the surface area of contact of the adhesive joint can be measured easily. Determination of adhesive strength becomes considerably more difficult when the adherend is a natural or synthetic fibre since the adhesive strength of a large specimen would be greater than the tensile strength of the fibre. The area of contact of the adhesive and the fibre surface must be kept small, therefore, but at the same time must be capable of accurate measurement.

Thus in measuring the adhesion of hairspray resins to hair fibres a technique must be used in which the fibres are introduced into a resin block so that the fibre is bonded along a given, measurable length. Such a technique has been developed by Shiryaeva, Gorbatkina and Andreevskaya (7) for the measurement of adhesive strength to glass fibres. This technique was adapted for use in the present study.

Experimental

A 10% w/w solution of hairspray resin was allowed to evaporate in a flat circular silicone rubber mould to yield a resin film about 300 μm thick. The dried film was cut into strips about 1 mm wide and 10 mm long while the film was still soft and flexible, and a small amount of the polymer

solution was applied to one side of two of the polymer strips. A single hair fibre was placed between and across the two strips, placed one on top of the other, so that it became cemented into a solid block of resin. Care was taken to ensure that the resin solution did not run along the fibre; the use of a fairly viscous solution helped to prevent this. In this way the fibre was coated with resin only over the width of the resin strip, i.e. about 1 mm. About 25 specimens were prepared for each resin studied. *Fig. 1* shows a completed specimen before testing.

The adhesion test specimens were left to dry for a few days and then the total surface area of adhesive bonding was measured for each specimen. The diameter of the fibre was measured by observation of the fibre cross-section under the microscope using an image splitting eyepiece (8). In order to do this the fibre was cut close to the point at which it emerged from the resin block on the side furthest from the root of the fibre and the end section at this point was examined. Owing to the well-known ellipticity of the hair fibres it was not considered sufficient to measure just one diameter. Instead the maximum and minimum diameters ($2a$ and $2b$) were measured and the circumference of the fibre calculated using the equation for the circumference of an ellipse:

$$\text{Circumference} = 2\pi\left(\frac{a^2+b^2}{2}\right)^{\frac{1}{2}}. \qquad (1)$$

The total surface area of the bond was then calculated by multiplying the circumference by the bonded length l. This bonded length was measured using a travelling microscope.

This method of measuring the bonded surface area took no account of the surface roughness of the fibres. It has not been possible to measure the true area of contact and all of the measurements are based on the assumption of a smooth-surfaced fibre.

After drying for 14 days the specimens were mounted in the jaws of an *Instron* tensile tester and extended at a constant rate of 15 mm min^{-1}. The load required to break the adhesive bond (F) was recorded and the adhesive strength of the specimen calculated from the formula:

$$\sigma_{ad} = \frac{F}{S} \qquad (2)$$

where σ_{ad} is the specific adhesion in kg cm^{-2}, F the load required to break the bond and S the surface area of the bond.

When testing the specimens the fibre was always pulled in the same direction; that is, the root end of the hair fibre was held in the lower pair of jaws and the resin in the other pair. In this way the motion of the fibre was with, and not against, the cuticle cells. This corresponds to the action of combing or brushing the resin out of the hair, when the resin is pulled away from the hair fibre by the comb moving towards the tip of the fibre.

On examining the specimens under the microscope after testing, a hole was usually clearly visible in the resin block where the fibre had been cemented (see *Fig. 2)* and no resin was left adhering to the fibre. This showed that the breaks were adhesive in nature.

Through all the tests a consistent behaviour was observed. In each case the specimens either broke down by adhesive failure at the resin-fibre interface or the adhesion was so great that the bond remained stable up to loads at which fibre breakage occurred. This latter behaviour was observed in a few cases where thin fibres and large bond lengths were encountered, but no examples of resin material fracture itself were observed. This is consistent with the observations of Hearle and Newton (3) on model systems of bonded fibres in their investigations on nonwoven fabrics.

Results

The value of adhesive strength for a particular resin was determined by taking the arithmetic mean of about 25 specimens. *Fig. 3* shows a typical set of results for hair spray resin C plotted as surface area of bonding against specimen break load. Although there is scatter in the results, as with all adhesion measurements, the correlation between surface area and break load can be clearly seen. The larger the bonded surface area the greater the break load of the specimen.

Fig. 4 shows the same data plotted as a distribution curve of adhesive bond strength against frequency. The frequency, Δn, is the number of specimens with strengths within a given interval. The specific adhesion was divided into intervals of 2.5 kg cm^{-2} and the resulting frequencies referred to the midpoints of the intervals.

Several commercially available hair spray resins were studied by the above method. *Table I* lists the adhesive strengths of these resins together with the number of specimens used in each case, and the average total surface area of the bonds, S. The final column of *Table I* lists the glass transition temperatures (T_g) for each of the resins.

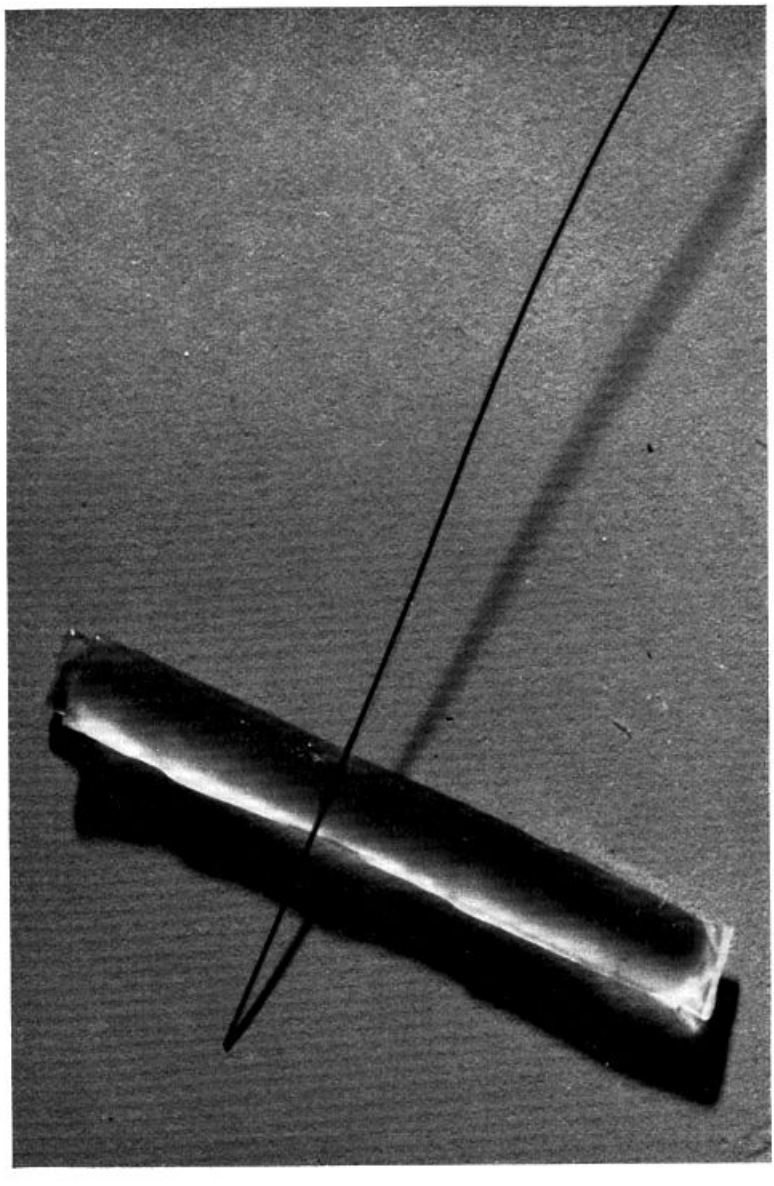

Figure 1. Completed adhesion test specimen before testing. ×7.

(*Facing p.* 300)

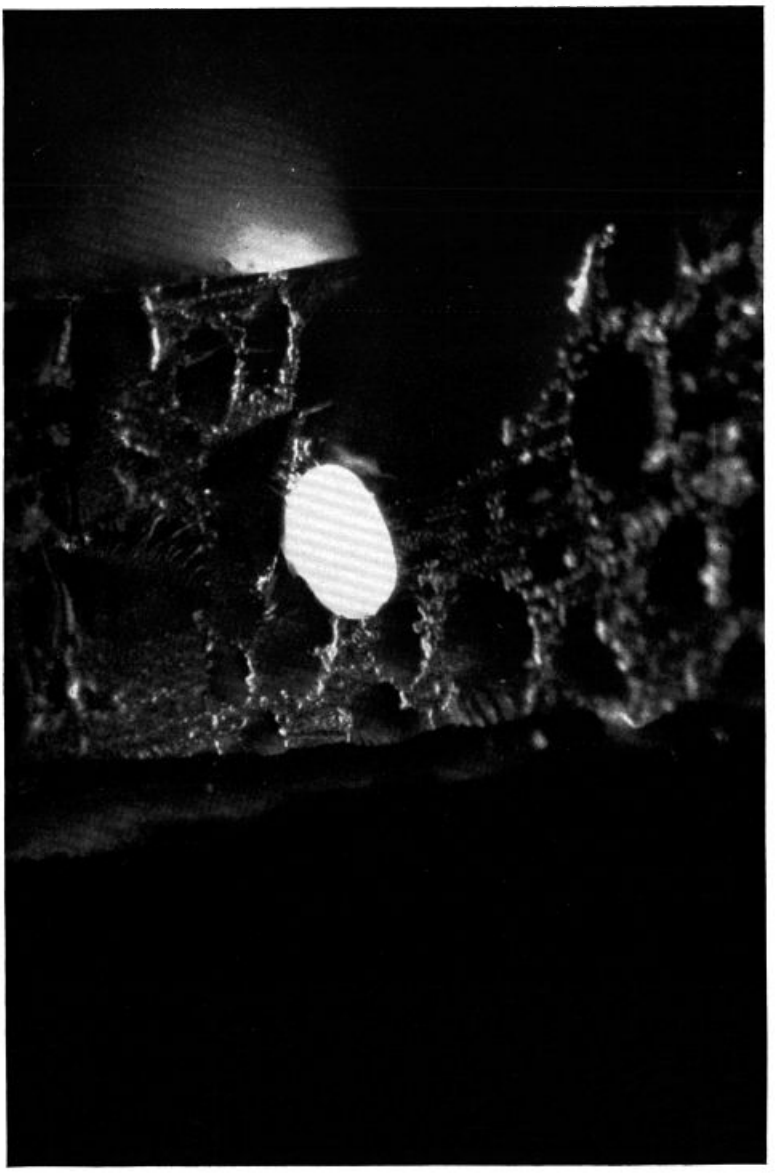

Figure 2. Resin block after withdrawing the hair fibre in the adhesion test. Adhesive break. (View from above.) × 200.

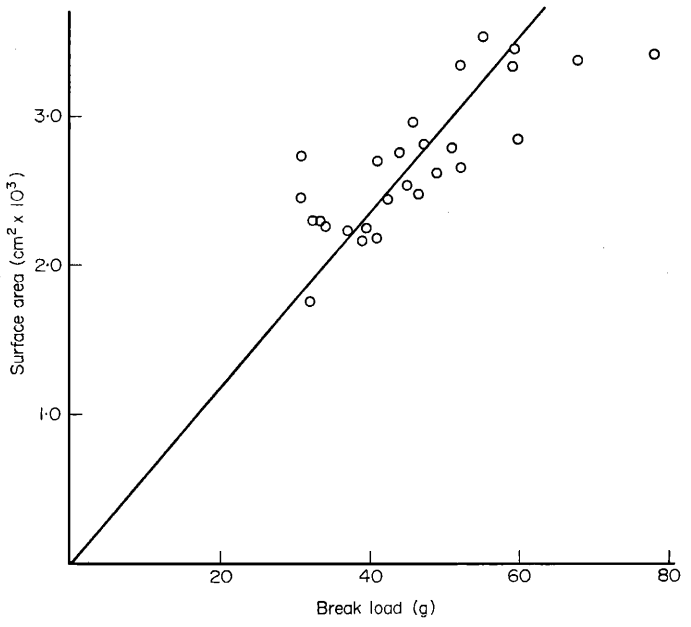

Figure 3. Results of adhesion test on 27 specimens of resin C. Plotted as surface area of bond against break load.

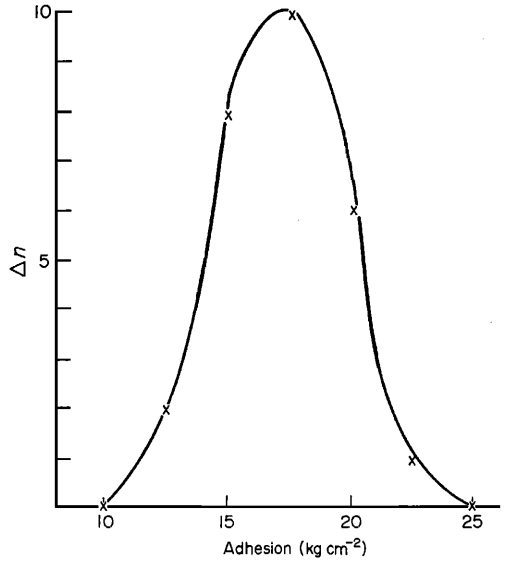

Figure 4. Adhesion of resin C to hair fibres. Adhesive strength distribution curve. (The frequency, $\triangle n$, is the number of specimens with strengths within a given interval. The adhesion was divided into intervals of 2.5 kg cm^{-2} and the resulting frequencies referred to the midpoints of the intervals.)

Table I. Experimental results for adhesion of hair sprays to hair fibres

Resin	S_{av} ($cm^2 \times 10^3$)	No. of specimens	σ_{ad} (kg cm^{-2})	T_g (°C)
E	2.88	29	21.8±3·3	24
H	2.88	22	18.9±2.9	32
D	2.88	26	18.5±2.5	40
C	2.68	27	17.1±2.5	47
F	2.85	24	16.8±3.3	—
A	3.01	21	16.6±3.6	42
I	2.57	28	15.4±2.2	59
B	3.05	25	15.0±1.9	51
G	2.80	27	14.5±2.7	34

It is interesting to consider the relationship between the adhesive strengths and the glass transition temperatures of the resins. This relationship is shown in *Fig. 5*. It will be seen that generally the softer resins (lower T_g) have the higher adhesive strengths.

Another relationship worthy of consideration is that between the adhesive strength of the resin and the viscosity of its solution. *Table II* shows the viscosities of certain of the resin solutions in ethanol at 40% w/w concentration. These measurements were carried out using a Ferranti cone and plate viscometer.

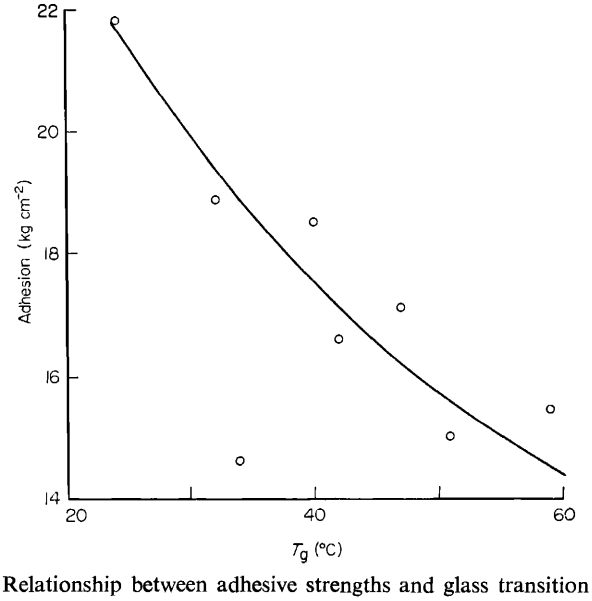

Figure 5. Relationship between adhesive strengths and glass transition temperatures (T_g) of hair spray resins.

Table II. Comparison between adhesive stengths of resins and the viscosities of 40% w/w solutions of the resins in ethanol

Resin	Adhesive strength (kg cm^{-2})	Viscosity at 40% w/w (cP)
E	21.8	360
D	18.5	450
B	15.0	450
C	17.1	630
F	16.8	925
G	14.5	1900

Discussion

The importance of fibre wettability and adhesion of resin to the fibres is now well accepted in the fabrics field. In view of the similarity between hair spray action and the formation of bonded fabrics it seems useful to consider such factors in the hair spray situation. Wettability and spreading have been considered in a previous communication (19) and adhesion of hair spray resins to hair fibres has been the subject of the present study.

Previous work by several authors on the adhesion of high polymers to such substrates as cellulose give useful indications as to the explanation of the present observations. Thus, McLaren (9) found that other things being equal (e.g. dipolarity and chemical composition of the polymers) the lower the viscosity of a material the more likely will it remain adapted to the interface during evaporation of the solvent. The lower the viscosity the more will the adhesive forces predominate over the cohesive forces within the adhesive which would tend to disrupt dipole-dipole attraction at the interface (10, 11). The transition from a solution of resin to a condition of solvent-free resin involves large dimensional changes and the material must possess sufficiently low viscosity at relatively high resin concentrations in order to remain in intimate contact with the surface during evaporation (12).

Inspection of *Table II* shows that in the main these trends are borne out by the experimental data. The lower the viscosity of the solution the stronger the adhesive joint.

'Deformability' proposed by McBain and Lee (13) expresses a highly

desirable property of an adhesive. Deformability of the dried resin film enables the joint to withstand impact or bending. Deformability during drying is important to the formation of strong joints. During drying internal stresses can be set up in the adhesive material if it is not deformable. The stresses are formed by the volume changes and when the joint is subsequently stressed it can, in extreme cases, fly to pieces.

If we can assume that deformability is related to the softness of the resin as measured by the glass transition temperature, then the above trend is also borne out by the present experimental data.

The surface of an adherend is rarely perfectly smooth but has numerous small interstices. For complete wetting of the surface by the adhesive these interstices must be filled by the liquid. Polymer-solvent mixtures often become viscoelastic solids even with as much as 15% of solvent remaining and with further loss of solvent the mixture passes through its glass transition temperature. Stresses then begin to arise at the adherend/adhesive interface and these stresses diminish the external force required to break the adhesive joint.

In the case of incomplete wetting of the adherend surface some of the interstices are not filled with adhesive before the mixture passes through its glass transition temperature. The stresses are then localized at the edges of these interstices. The lower the viscosity of the adhesive mixture the faster the spreading and the easier it is for the interstices to be filled.

When the adhesive completely wets the adherend before it passes through its glass transition temperature, the stresses are not localized at the edges of the interstices and a stronger joint results. It follows that low viscosity and low glass transition temperature both promote good adhesion.

A commercial application of the above principles has been demonstrated by Alexander (14). It was shown that polymethyl methacrylate and polystyrene can render wool unshrinkable if the correct quantity of plasticizer is present. The concentration of plasticizer was found to be critical. Starting with pure resin the shrinkage of wool decreased from 31.8% to 5.4% at 30% diethyl phthalate content and then rose again as more plasticizer was included. Similarly copolymers of butadiene and methyl methacrylate, within a narrow range of compositions, were capable of producing excellent non-shrinkability, while the two homopolymers, and copolymers of the wrong composition, did not produce the effect. The physical properties of the polymer obviously play a vital part in obtaining the desired effects and the polymer must be neither too hard and brittle, nor too soft and rubbery.

Conclusions

The technology of non-woven bonded fabrics and of the production of fabrics with anti-felting properties may be usefully compared to the processes occurring when hair sprays are applied to hair. Thus, Möschler (15) and Tikhomirov (16) have both demonstrated that the production of bonded fabrics involves the formation of resin bridges between fibres and at fibre intersections.

The resin bonds in non-woven fabrics can be formed in the same manner as those formed when using a hair spray, i.e. from a solution of the resin, or by alternative techniques such as the use of polymer melts or aqueous dispersions.

Various workers have attempted to characterize the types of bonding found in bonded fabrics (17, 18). There appear to be three main types of bond; simple, parallel and complex (17). The simple bonds involve only two fibres, approximately at right angles; parallel bonds involve two fibres bonded side by side, while complex bonds involve more than two fibres which are sufficiently close to be included in the same resin bond.

Measurements of adhesion of hair spray resins to hair fibres have shown that for several commercially available resins the adhesive strengths are in the range 14–22 kg cm^{-2}. Tikhomirov and Gusev (4) have reported the value 40.1 kg cm^{-2} for the adhesion of epoxy resin to wool fibres.

Certain general trends are noticeable from the results. For example, the greatest adhesion is found for resins which give solutions of lower viscosity. This is in agreement with previous observations on the adhesion of high polymers to such substrates as cellulose and it is considered essential that a good adhesive should have a low viscosity in solution in order that the resin remains in intimate contact throughout the dimensional changes accompanying the loss of solvent. Intimate interfacial contact is essential for good adhesion since the adhesive bonds act only over very small distances.

Similarly the adhesive strength shows a general increase with the softness or deformability of the resin. Again reference to earlier adhesion studies shows that deformability allows stresses, set up on drying of the adhesive, to be dissipated. If such stresses cannot be dissipated they may cause shattering of the joint when any subsequent stress is applied. Deformability is also needed to allow flexing or bending of the joint. This latter condition will promote lasting hold in a hair spray.

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Relative merits of 'in use' and laboratory methods for the evaluation of antimicrobial products

R. A. COWEN*

Presented on 13th November 1973 in Nottingham at the Symposium on 'Evaluation of Product Performance', organized by the Society of Cosmetic Chemists of Great Britain.

Synopsis—The relationship between the resistance of cultures grown in the laboratory and on the skin is examined in the light of factors known to influence RESISTANCE OF BACTERIA under laboratory culture. Examples are taken from tests designed to measure the efficacy of HAIR SHAMPOOS, DEODORANTS, BATH ADDITIVES and ANTISEPTICS to show that little correlation exists between activity measured in the laboratory and in practice. Both LABORATORY TESTS and 'IN-USE' TESTS should be carried out side by side as a means of identifying factors which influence the results. With this information design of more realistic tests should be possible.

INTRODUCTION

The methods used for the evaluation of the antimicrobial activity of a product can be divided into three groups.

Simple laboratory tests.

Simulated 'in-use' tests.

In-use tests.

The latter, by definition, refer solely to the evaluation of the product under conditions of usage and not for the description of other types of

* Bacteriological Laboratory, Pharmaceutical Division, Reckitt and Colman, Dansom Lane, Hull.