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Polymer Properties Influencing Curl Retention at High Humidity

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Synopsis—Various test procedures to determine the high-humidity properties of hair spray resins are described. The polymers included in this investigation are: carboxylated polyvinyl acetate, polyvinylpyrrolidone, polyvinylpyrrolidone/vinyl acetate copolymer, dimethyl hydantoin-formaldehyde resin, and several experimental resins. The data presented illustrate the relationship of curl retention at 90% RH with: equilibrium moisture content, hydrophilic/hydrophobic functionality, molecular weight, moisture vapor transmission, film hardness, tensile strength, and elongation. The effect of neutralization with 2-amino-2-methyl-1,3-propanediol (AMPD) on these properties is discussed for some carboxylated polymers. The various procedures brought together from several technologies are adaptable to testing of hair spray formulations.

Introduction

It is the purpose of this paper to show how the choice of polymer and the variation in polymer properties are related to curl retention. The test procedures to be discussed are: high-humidity curl retention, moisture transmission (liquid), moisture transmission (vapor), equilibrium moisture content, film hardness, tensile strength, and elongation.

It must still be determined to what extent these test results correlate with the properties of hair spray preparations desired by the consuming public. Further work in this laboratory will seek to provide the answer to the existence of such relationships.

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In addition to providing an evaluation of polymer properties, these test techniques appear to lend themselves to evaluation of formulation variables of a single resin system. That is, the procedures described might be used to determine the change in high-humidity properties upon addition of plasticizers, perfumes, or other functional additives.

EXPERIMENTAL

Curl Retention

A constant relative humidity atmosphere was obtained in a Tenney Environmental Chamber (Model TH-10)* which was modified by replacing the door with a Lucite®† window (Fig. 1). The temperature was maintained for all retention tests at 22°C and a relative humidity of 90 ± 2%.

Hair swatches were prepared by binding at the root end approximately 2 g of Remi-Blue String European hair. After washing with a commercial shampoo and thoroughly rinsing with distilled water, the hair swatch was cut to measure 25.4 cm in length.

Test specimens were prepared by suspending the curl swatch from a motor chuck which was adjusted to rotate at a constant speed of 20 rpm. The end of the curl was weighed with a 10-g clip to prevent motion of the hair during spraying. With the hair rotating, the hair spray formulation under test was sprayed onto the swatch for 10 seconds from a distance of 15 cm. Excess resin was removed by gently bringing the thumb and forefinger down the length of the curl. The moist swatch was then combed twice, wound on a 1.26-cm Teflon®† rod, removed, and secured with a hair clip. All test samples were dried at 60°C for 30 minutes, then conditioned for at least 16 hours at 22°C and 50% relative humidity. A minimum of ten swatches was prepared for each parameter level of formulation investigated. After conditioning, the curls were unwound into a spiral and placed at random on vertical Lucite® retention panels (Fig. 2). The panels were marked to permit measurement of curl length to the nearest 0.6 cm.

After initial curl lengths were recorded, the panels were placed in the humidity chamber. The changes in curl lengths were then recorded at 30-minute intervals over a period of three hours. In most instances, there is an initial rapid decrease in curl retention and then a much slower loss of curl after approximately 120 minutes.

* Tenney Engineering, Inc., Union, N. J.

† Lucite and Teflon are registered trademarks of E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

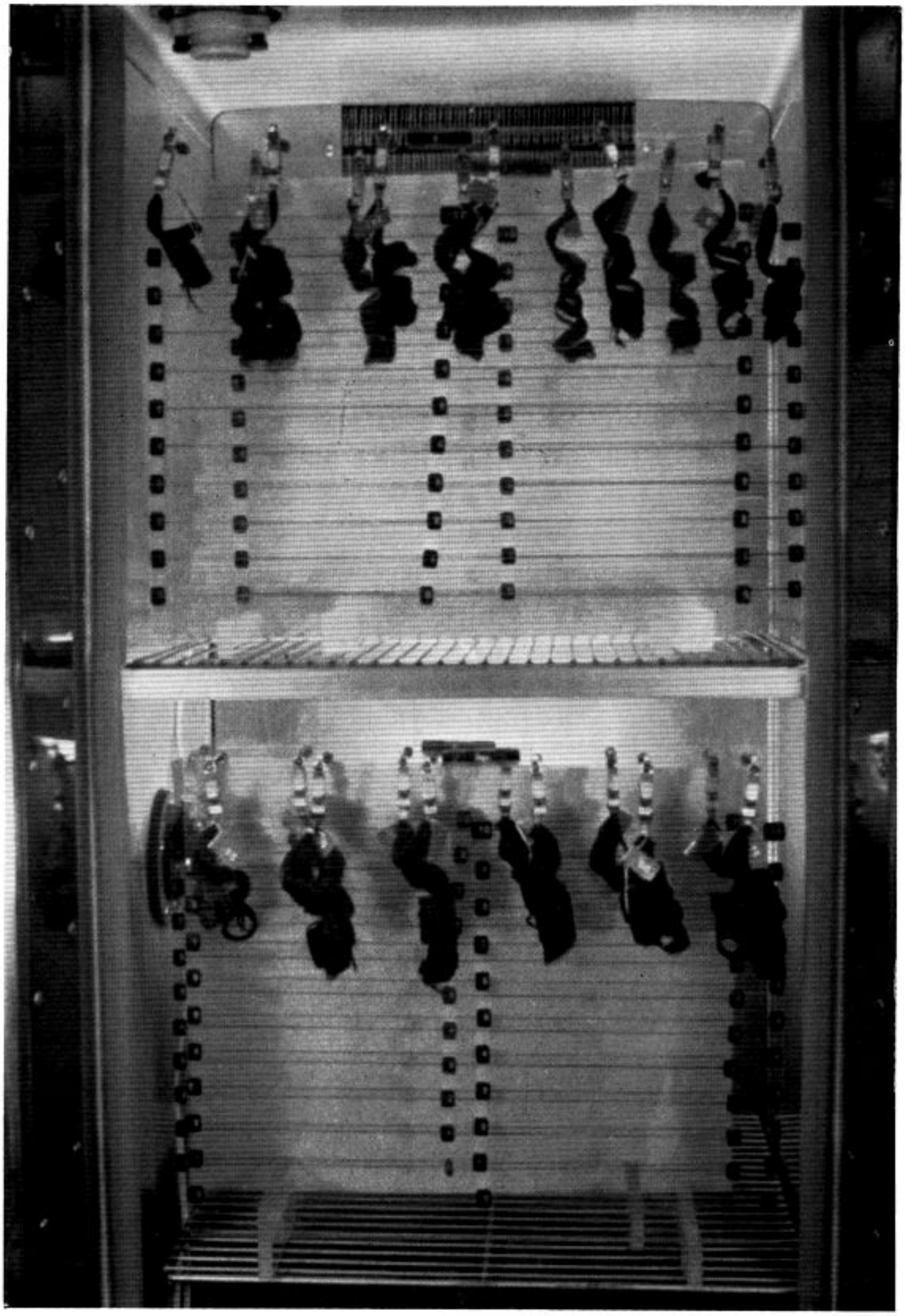

Figure 1. Modified Tenney environmental chamber containing a set of curl swatches

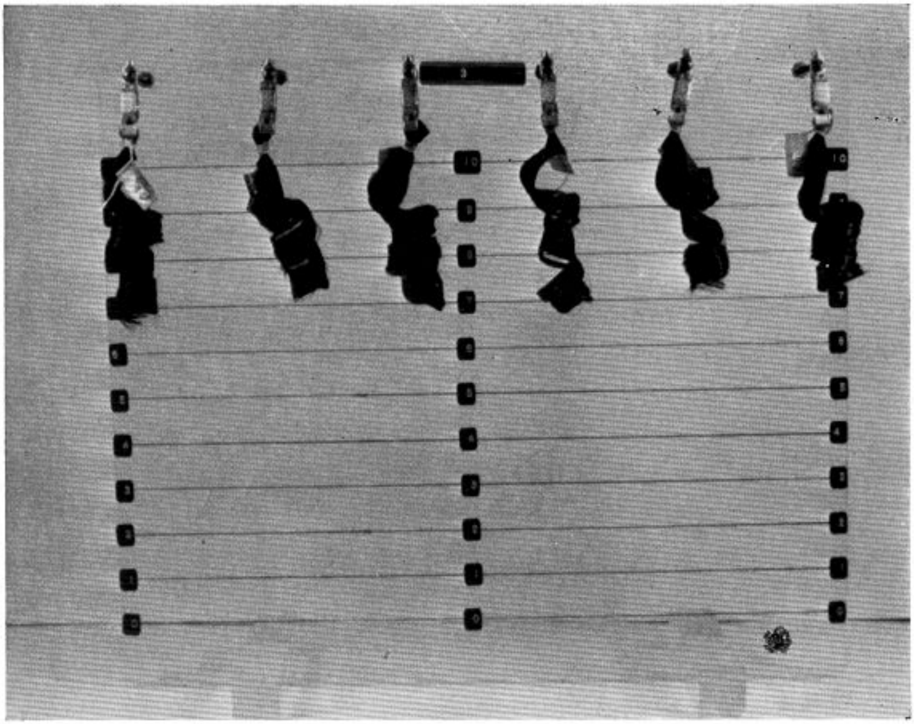

Figure 2. Lucite retention panel

The percentage of curl retention was calculated from equation 1.

$$\text{Curl retention (\%)} = \frac{L - L_t}{L - L_0} \times 100 \qquad (1)$$

where:

L = length of hair fully extended (25.4 cm)
L_0 = length of hair before exposure
L_t = length of curl after exposure at time (t)

Standard statistical methods were used to interpret the significance of all observations.

Moisture Transmission (Vapor)

The moisture vapor transmission rates (MVTR) of various polymeric substances were determined at 90% relative humidity at 22°C. Films were cast from anhydrous ethanol on super calendered Kraft paper and sealed on MVTR cups containing anhydrous Drierite* to absorb

* W. A. Hammond Drierite Co., Xenia, Ohio

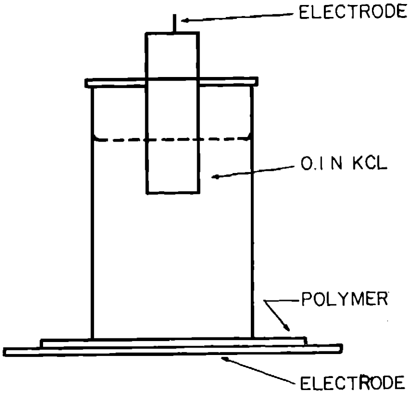

Figure 3. Schematic diagram of transmission apparatus illustrating the electrolytic cell and the polymer/electrode relationship

moisture penetrating the film. The particular paper chosen was known to offer no barrier to moisture; therefore, the MVTR of the paper/polymer construction can be considered to be the MVTR of the polymer alone. After drying at 60°C for two hours, and 15 minutes at 105°C, and conditioning for 24 hours at 60% RH at 22°C, the test samples were weighed and placed in the high-humidity environment. Weights were taken periodically to determine the rate of water pickup. MVTR is expressed as milligrams of water/square centimeter of polymer film/second/centimeter thickness ($mg/cm^2/sec/cm$).

Moisture Transmission (Liquid)

Test samples were prepared from a 40% ethanol solution by casting a 0.0038-cm wet film on a tin plate. The films were air dried for 16 hours at 22°C, then desiccated for 24 hours. Resistivity measurements were conducted at 22°C.

Figure 3 shows a schematic of the transmission apparatus. The upper electrode was connected to a power source* while the lower electode or tin substrate led to an electrometer.† Finally, a recorder,‡ activated by the electrometer continuously plotted the change in resistivity, which is a measure of the liquid moisture transmission.

Tensile Strength and Per Cent Elongation

Test specimens were free films deposited from anhydrous ethanol solutions on a paper coated with a silicone release agent. All films

* Model #9020-5, Sorensen & Co., South Norwalk, Conn.
† Model #602, Solid State Electrometer, Keithley Instruments, Cleveland, Ohio.
‡ Model #VOM-5, Bausch & Lomb, Rochester, N. Y.

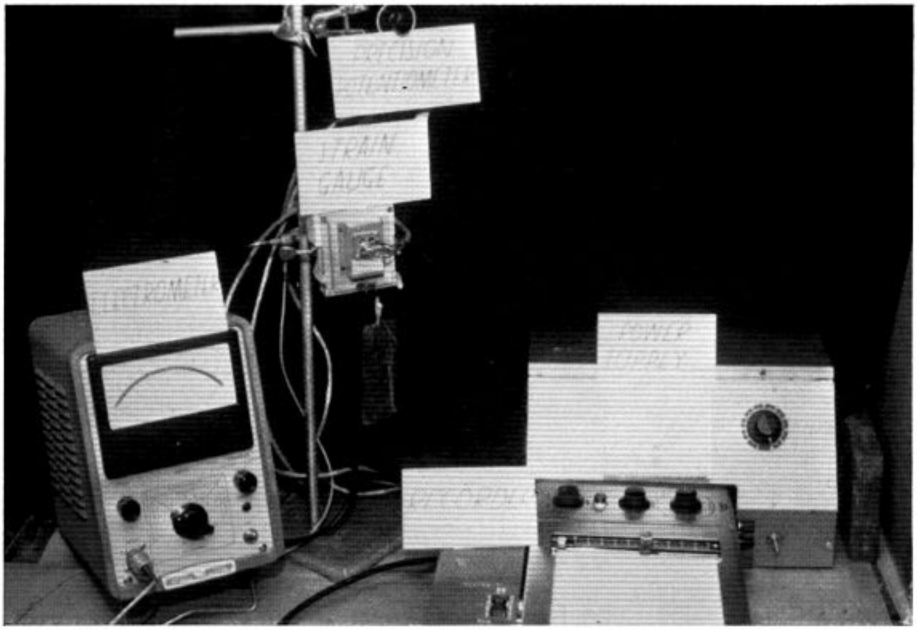

Figure 4. Strain gauge apparatus

were dried slowly and thoroughly to prevent air or solvent entrapment. The dried films were approximately 0.0038 cm in thickness. From these, tensile pieces were cut in 1.26-cm wide strips, conditioned, and tested at 90% RH at 22°C on an Instron Model TM* at a crosshead speed of 0.5 cm/min.

Equilibrium Moisture Content

The equilibrium moisture content was determined on free films cast from anhydrous ethanol. The films were air dried for 2 hours at 22°C, 2 hours at 60°C, 15 minutes at 105°C, and then stored in a desiccator for 24 hours. The dried films were attached to a nulled pressure transducer or strain gauge (Fig. 4). A pressure transducer will convert mechanical motion or strain into electrical current when a stress changes the resistivity of one leg of the transducer circuit. The dry film weight was recorded as millivolts on the readout of a DC-Micro-Volt Ammeter (Model 425A†). The film weight was then nulled by the precision potentiometer and the strain gauge assembly was inserted into an atmosphere of 90% RH at 22°C. The increase in weight was

* Instron Corp., Springfield, N. J.
† Hewlett Packard Corp., Paramus, N. J.

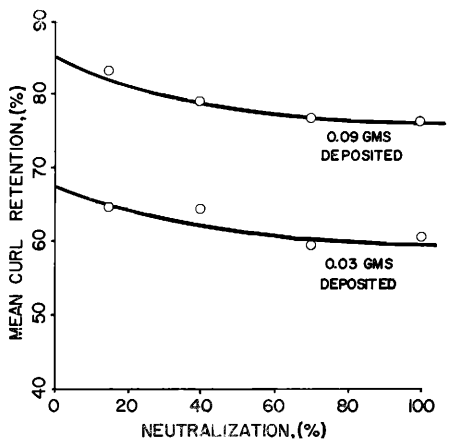

Figure 5. Curl retention *vs*. neutralization with AMPD (2-amino-2-methyl-1,3-propanediol) for Polymer B after 30 minutes at 90% RH (22°C)

continuously recorded as a change in voltage. The equilibrium millivolt deflection could be converted to grams and the equilibrium moisture content calculated as:

$$\frac{\text{Grams water}}{\text{Grams polymer}} \times 100 \qquad (2)$$

Film Hardness

The relative hardness of films was determined with a Sward Rocker* apparatus. This device is set into a rocking motion on the film under test and the number of complete, standardized rocking cycles is counted. The value or number assigned is relative to glass which has an arbitrary value of 100. Therefore, the higher the Sward number the harder the film. Soft, tacky films have a Sward reading of zero.

Results

Statistically designed experiments were conducted to determine the effect of neutralization with 2-amino-2-methyl-1,3-propanediol (AMPD), molecular weight, functionality, and copolymer composition upon curl retention, moisture permeability, tensile strength, and film hardness. Additionally, this study included various types of resins: carboxylated polymers, polyvinylpyrrolidone,† a polyvinylpyrrolidone/vinyl acetate copolymer,† and dimethyl hydantoinformaldehyde resin.‡

* Gardner Laboratory Inc., Bethesda, Md.

† PVP, PVP/VA, General Aniline and Film Corp., New York, N. Y.

‡ Dantoin 734, Glyco Chemicals, Div. of Chas. L. Huisking Co., Williamsport, Pa.

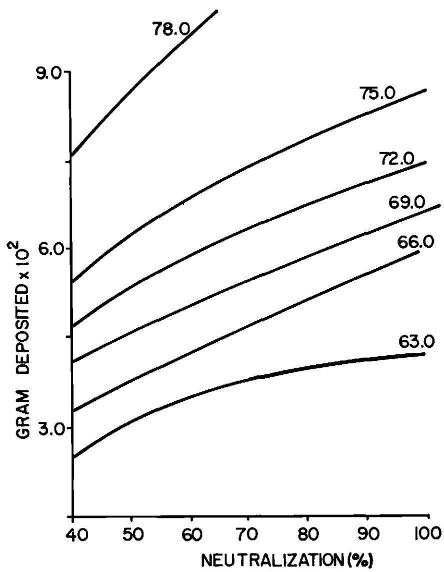

Figure 6a. Iso-curl retention lines for Polymer B after 30 minutes at 90% RH (22°C)

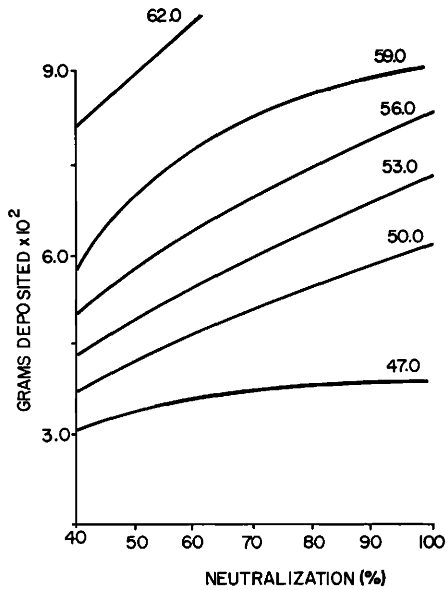

Figure 6b. Iso-curl retention lines for Polymer B after 180 minutes at 90% RH (22°C)

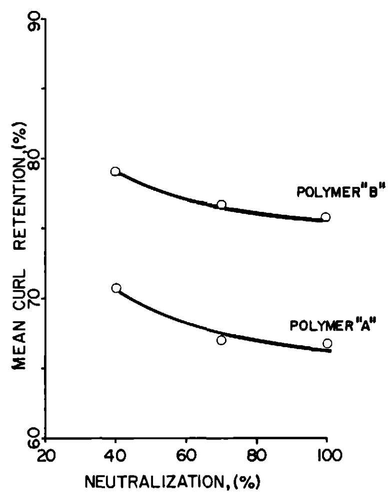

Figure 7. Curl retention *vs.* neutralization with AMPD for Polymer A and Polymer B with 0.09 g of resin deposited per swatch after 30 minutes at 90% RH (22°C)

A carboxylated vinyl acetate copolymer (Polymer A)* was compared with an experimental carboxylated vinyl acetate terpolymer (Polymer B) which was specially prepared to include a hydrophobic monomer.

* RESYN 28-1310, National Starch and Chemical Corp., New York, N. Y.

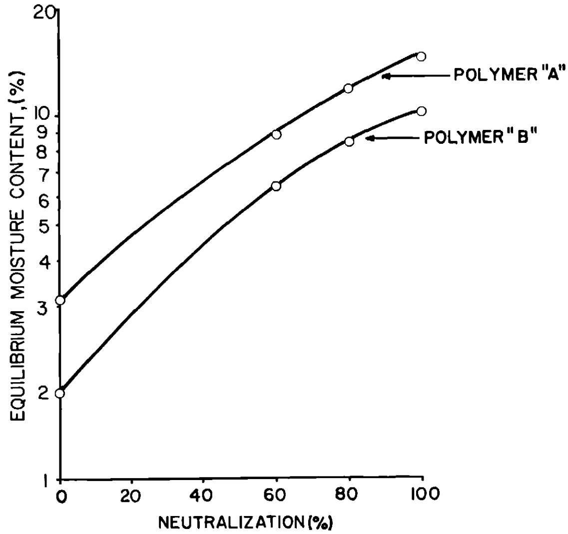

Figure 8. Equilibrium moisture content at 90% RH for Polymer A and Polymer B *vs.* neutralization with AMPD (22°C)

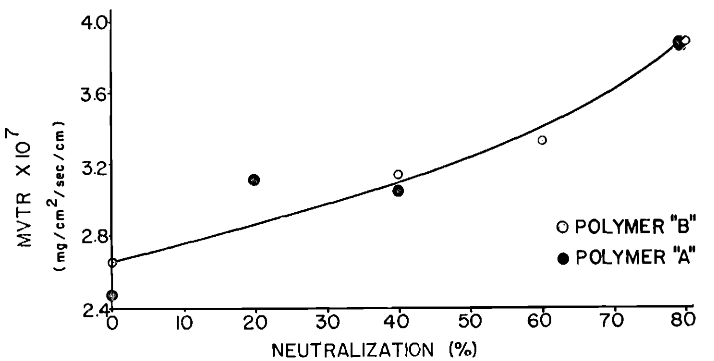

Figure 9. Moisture vapor transmission rate (MVTR) at 90% RH *vs.* neutralization with AMPD for Polymer A and Polymer B (22°C)

The mean curl retention of Polymer B varied as the neutralization and deposition weight was altered (Fig. 5). It can be seen that both neutralization and deposition weight have an effect on curl retention. Increasing neutralization tends to decrease curl holding ability; increasing polymer deposition on the hair offers a significant increase in retention. An alternate method of illustrating the data is shown in Figs. 6a and 6b. A system of iso-retention lines was constructed so

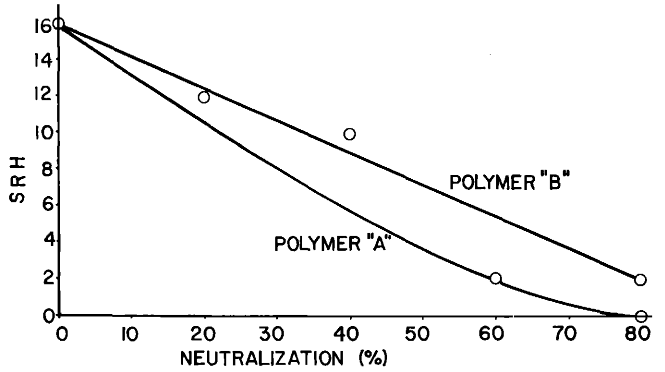

Figure 10. Sward Rocker hardness at 90% RH *vs.* neutralization with AMPD for Polymers A and B (22°C)

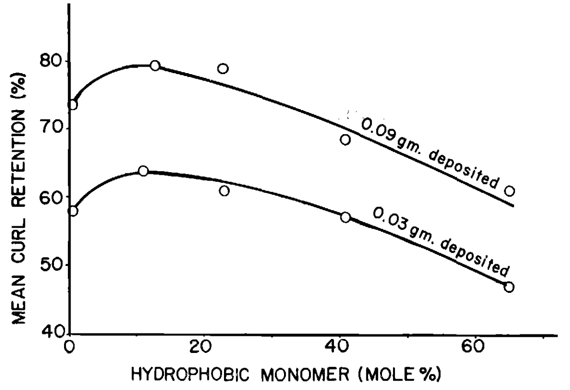

Figure 11. Curl retention at 90% RH for carboxylated vinyl acetate terpolymers containing increasing amounts of hydrophobic monomer. Neutralized 40% with AMPD at 30 minutes exposure (22°C)

that the three coordinates—deposition weight, neutalization, and exposure time—might be visualized. Each system of lines might be considered a plane or slice removed from the three-dimensional surface generated by the three coordinates.

The relationship demonstrated with the iso-retention lines might be clarified with one specific example. From Fig. 6a, it can be seen that at a deposition of 0.06 g of resin (50% neutralized), the mean retention was 75%. By extrapolation, a deposition weight of 0.075 g (75% neutralized) will also result in 75% retention.

A comparison of Polymer A and Polymer B (Fig. 7) demonstrates the improved high-humidity curl retention achieved by including the

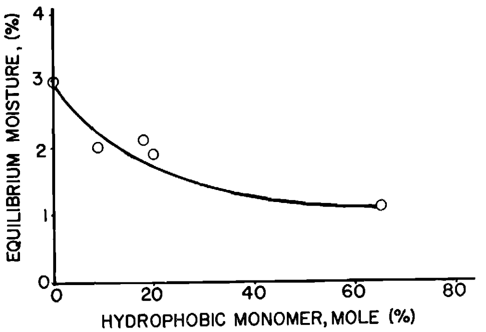

Figure 12. Equilibrium moisture content at 90% RH for carboxylated vinyl acetate terpolymers with increasing amounts of hydrophobic monomer (22°C)

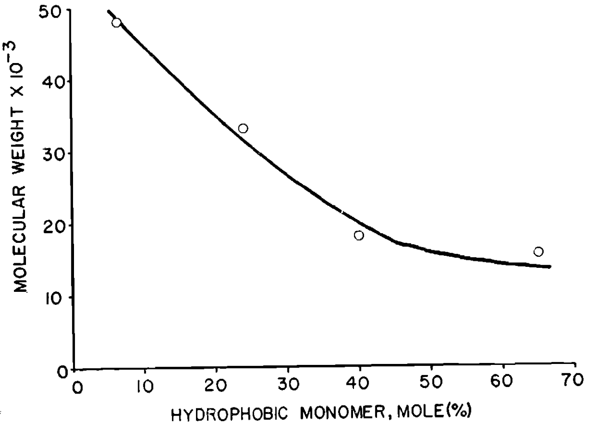

Figure 13. Molecular weight as a function of carboxylated vinyl acetate terpolymer composition

hydrophobic monomer. The relationship of equilibrium moisture content *vs.* neutralization for Polymers A and B (Fig. 8) indicates the same relative improvement observed with curl retention.

The incorporation of a hydrophobic moiety in the polymer structure enhances the curl retention at high humidities and decreases the equilibrium moisture content of the polymer. It is apparent that this relationship holds true over the complete neutralization range of the carboxyls in the polymer structure. It was also found that the moisture vapor transmission rate (MVTR) of the carboxylated polymers increases with increasing neutralization (Fig. 9). This latter relationship shows that, notwithstanding the inclusion of a hydrophobic moiety into the

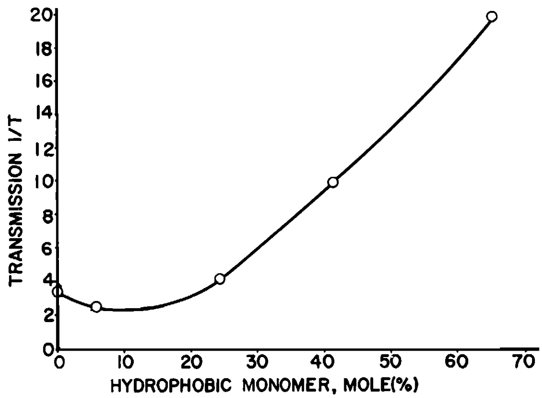

Figure 14. Moisture transmission relative to increased hydrophobic monomer incorporated into carboxylated vinyl acetate terpolymers (22°C)

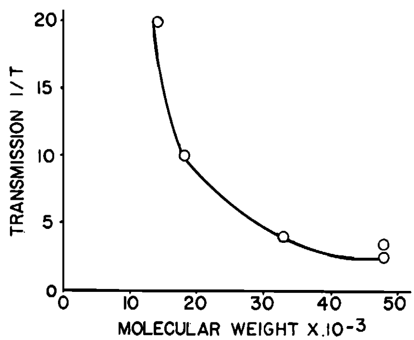

Figure 15. Moisture transmission as a function of the molecular weights of the polymers illustrated in Fig. 14 (22°C)

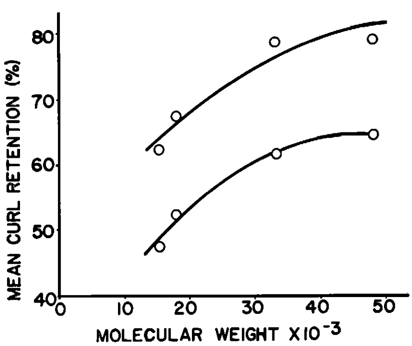

Figure 16. Curl retention at 90% RH as a function of molecular weight for a series of carboxylated vinyl acetate terpolymers. Upper curve, 40% neutralization with AMPD; Lower curve, 100% neutralization with AMPD, 0.06 g deposited and 30 minutes exposure (22°C)

polymer, the moisture vapor transmission rate is unchanged. That is, both polymers increase in transmission rate with increasing neutralization.

The film hardness (Sward Rocker hardness) of the polymers changes as a function of carboxyl neutralization (Fig. 10). It is apparent that the film hardness is increased slightly (but significantly) by inclusion of hydrophobic monomer, especially at higher neutralization ranges.

The effect of hydrophobic monomer was studied further by determining the effect of increasing amounts of the hydrophobic moiety upon curl retention (Fig. 11). It appears that there is an optimum composition with respect to this moiety that results in the best curl retention obtainable in this particular system. Further increase in the hydrophobic monomer seems only to detract from this property.

A marked decrease in the equilibrium moisture content of films was observed as the concentration of hydrophobic monomer was increased (Fig. 12). Also, as the hydrophobic moiety was increased, a dramatic decrease in the molecular weight of the polymer was observed (Fig. 13). This molecular weight decrease was due to the particular choice of monomer and the polymerization conditions employed. When moisture permeability tests were run on these polymers with increasing hydrophobic monomer composition, their permeability rates decreased as the moiety was increased and then rose rapidly (Fig. 14). The relationships shown in Figs. 15 and 16 indicate a correlation between molecular weight and both moisture transmission and mean curl retention.

Another example of the effect of molecular weight was illustrated in a series of polyvinylpyrrolidone polymers. A highly significant change in curl retention can be achieved as the molecular weight is varied. This effect is shown in Fig. 17 where curl retention of PVP *vs.* molecular weight is plotted. Although improved (higher) curl retention is obtainable at higher molecular weights, the practical consideration of formulation viscosity and spray characteristics must be taken into account. As the molecular weight of a given polymer is increased, it becomes more and more difficult to obtain a suitable spray pattern from an aerosol container.

Further examination of the effect of hydrophilic functionality, as distinct from neutralization of carboxyl groups, was conducted with a series of copolymers containing various amounts of hydroxyl groups. A significant decrease in curl retention was observed as the percentage of the water and sensitive hydroxyl functionality was increased (Fig. 18).

Two interesting relationships for the carboxylated vinyl acetate

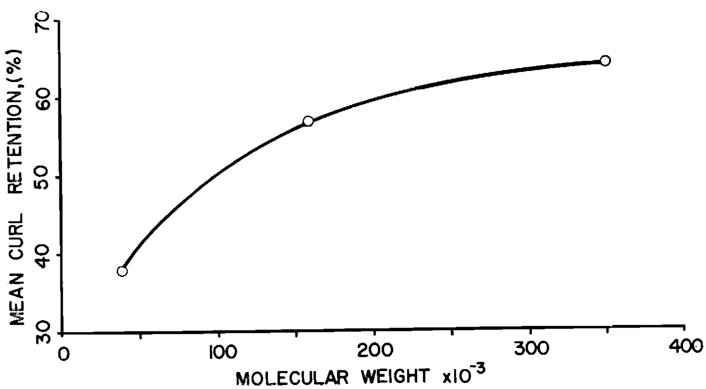

Figure 17. Curl retention after 30 minutes exposure at 90% RH *vs.* molecular weight of polyvinyl pyrrolidone, 0.06 g of resin deposited per hair swatch (22°C)

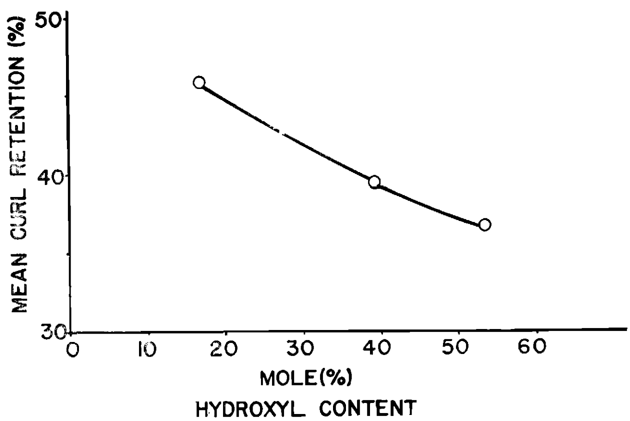

Figure 18. Curl retention after 30 minutes exposure at 90% RH *vs.* hydroxyl functionality (mole %) of copolymers, 0.06 g deposited (22°C)

copolymer are illustrated in Figs. 19 and 20. Tensile strength (psi) at 90% RH tends to decrease with increased neutralization, while elongation increases. These observations appear to be consistent with the reported changes in film hardness as the neutralization varies. Whereas unneutralized films are stronger and more brittle with higher Sward values, the films become weaker and softer as neutralization is increased.

A summary of commercial hair spray polymer properties is presented in Table I. Polymer B, not a commercial polymer, is included to illustrate the improved properties that may be achieved by polymer design. The data included in the table clearly show the relationship of curl retention and polymer properties at elevated humidity.

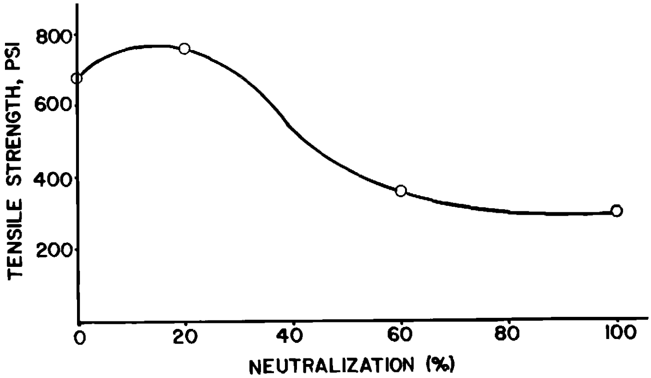

Figure 19. Tensile strength (psi) at 90% RH *vs.* neutralization with AMPD for Polymer A (22°C)

Table I
Polymer Properties of Commercial Resins at 90% Relative Humidity

Polymer	Mean Curl Retention (%) 180 Min	Equilibrium Moisture Content (%)	Moisture Vapor Transmission Rate (mg/ cm²/sec/cm)	Sward Rocker Hardness	Tensile (psi)
Polymer B (unneut)	63	1.5	2.6	16	1000
Polymer B (60% neut)	54	6	3.0	10	400
Polymer A[a] (60% neut)	49	9	3.4	4	360
Polymer A (100% neut)	46	14	3.8	0	230
DMHF	34	13	6.1	0	30
PVP/VA	33	38	4.7	0	200
PVP	28	45	6.9	0	200

[a] RESYN 28-1310, National Starch and Chemical Corp., Plainfield, N. J.

The resins are listed in order of decreasing curl retention. The correlation coefficients for a linear fit of curl retention *vs.* polymer properties are:

Equilibrium moisture content	−0.86
Moisture vapor transmission	−0.93
Sward Rocker hardness	0.88
Tensile strength	0.84

The anomalous relationship of the moisture absorption and curl retention for DMHF can be clarified by observing the high moisture

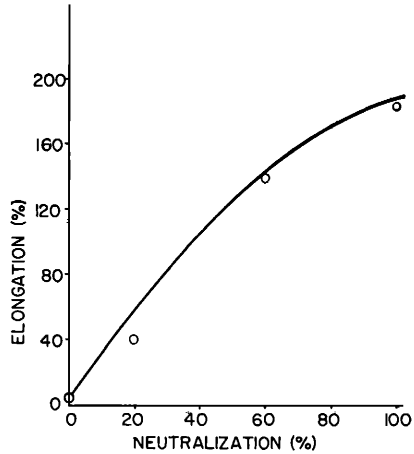

Figure 20. Elongation (%) at 90% RH *vs.* neutralization with AMPD for Polymer A (22°C)

transmission and extremely low tensile strength. On the basis of moisture absorption alone, one might expect DMHF to have a curl retention greater than 46%. But, in this polymeric system, the moisture transmission and tensile strength have a more significant effect than equilibrium moisture content.

SUMMARY AND CONCLUSIONS

It is evident from the data presented that curl retention at elevated humidity is related to the degree of neuturalization of carboxylated polymers, the hydrophobic or hydrophilic nature of the polymer, and, to a large extent, the average molecular weight.

The practical considerations of curl retention at high humidity should be examined in view of the data presented in Fig. 21 and Table I. The curl retention and high-humidity properties of various commercial hair spray resins are illustrated. It might be pointed out that these polymers offer a wide range of film properties. The more hygroscopic or water-sensitive polymers, such as PVP and PVP/VA, may be suitable primarily for soft-holding hair sprays or in formulations marketed in less humid areas. These limitations are not apparent when less moisture sensitive polymers are utilized. They have increased curl-holding power, and the resins can be incorporated into both hard-to-hold and soft-holding formulations notwithstanding the climatic conditions.

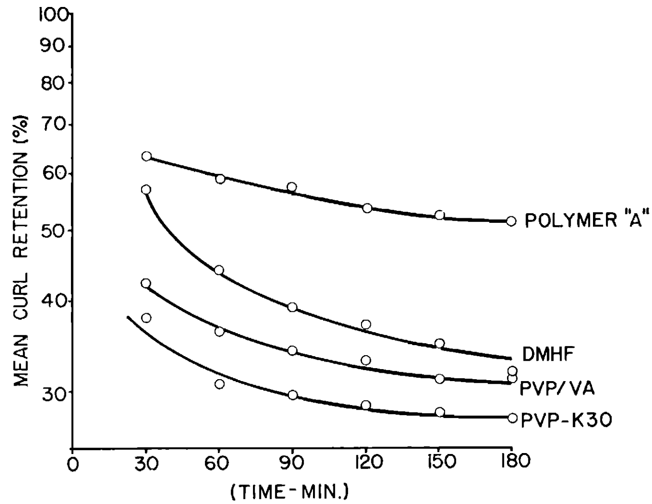

Figure 21. Curl retention at 90% RH as a function of time for several commercial hair spray resins (0.06 g deposited)

A most important property of the carboxylated polymers is their ability to be varied by reaction of the polymeric acidity. Film hardness, moisture transmission, tensile strength, and elongation, and ultimately curl retention may be modified to cover a wide range of applications.

For carboxylated vinyl acetate polymers, the following conclusions can be made from the data presented.

(*a*) Curl retention is inversely related to neutralization with AMPD.
(*b*) Moisture transmission rate is increased as the neutralization is changed from 0 to 100% of the theoretical acidity.
(*c*) Molecular weight affects the curl retention properties in a direct relationship, i.e., the higher molecular weight polymers exhibit higher retention at elevated humidity.
(*d*) Tensile strength and elongation are a function of degree of neutralization. The former property decreases as neutralization is raised, while the latter property increases.

In general, it may be concluded that the high-humidity curl retention of a given polymeric composition is a complex function of its equilibrium moisture content, moisture transmission rate, and tensile strength.

The foregoing is an attempt to correlate certain polymeric properties with one desirable characteristic of a hair spray formulation, namely curl retention. Obviously, such considerations as ease of combing, adhesion to the hair, gloss, and feel are all important to ultimate consumer acceptance which in the final analysis spells the success or failure of a commercial product.

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