J. Soc. Cosmetic Chemists, **17**, 595–605 (1966)

Hygroscopicity and Hardness of Hair Spray Resins at Varying Humidities

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Presented May 10, 1966, New York City

Synopsis—An apparatus is described for measuring moisture pick-up, drying rate, and Sward Hardness of various resin films at relative humidities of from 50 to 90%. Data are given on films laid down from anhydrous SDA #40 ethyl alcohol. Resins used include: Polyvinyl Pyrrolidone (PVP K-30), Vinylpyrrolidone/Vinyl Acetate Copolymer (PVP/VA 735), VEM® Resins, 90, 50, and 0% neutralized with 2-amino-2-methyl-1,3-propanediol (AMPD), and National Starch Resyn® 28-1310, 90, 70, and 0% neutralized with AMPD. One set of data used the unplasticized films, and a second set used the film plasticized with 3.5% DC-555 Silicone Oil. Although this apparatus has been useful for collecting data on resins used in hair sprays, the method and apparatus can be used for obtaining data with these and other resins for applications such as adhesives and coatings.

Introduction

There has been a noticeable lack of data comparing moisture pick-up and hardness of hair spray resin films at various humidities. What little data are available have been on work that was done only with one type of resin by the manufacturer using a method not fully described. One Technical Service Bulletin (1) shows the water absorption rate of Resyn®† 28-1310, neutralized 125, 90, and 0% with 2-amino-2-methyl-1,3-propanediol (AMPD), for periods of up to 160 hours. A patent (2) assigned to National Starch gives the Sward Hardness of Resyn 28-1310

* G. Barr Co., Niles, Ill. 60648.

† Resyn is a registered trademark of National Starch and Chemical Corp., Resin Division, New York, N. Y.

Figure 1. Controlled humidity chamber

neutralized to varying degrees with several different amino-alcohols. Sward Hardness values range from 44 down to 14, starting with unneutralized resin and going up to 150% of the theoretical equimolar amount of copolymer reacted. Another Technical Service Bulletin (3) describes the hardness of Resyn 28-1310 at varying degrees of neutralization with four different amino-alcohols. This bulletin also shows the moisture content at equilibrium with 50 to 90% relative humidity of Resyn 28-1310 films neutralized to 100, 80, and 60% with AMPD. These films were cast from solutions in anhydrous SDA-40 ethyl alcohol. The hygroscopicity of PVP K-30* (4) and PVP/VA (5) has been reported at relative humidities ranging from 30 to 90%.

About the only work comparing various resins using the same method was done in Japan (6). VEM®† −640, −645, and −649, PVP K-30,

* PVP K-30 and PVP/VA, Antara Chemicals, Division of General Aniline and Film Corp., New York, N. Y.

† VEM is a registered trademark of G. Barr Co., Division of Pittsburgh Railways Co., Niles, Ill.

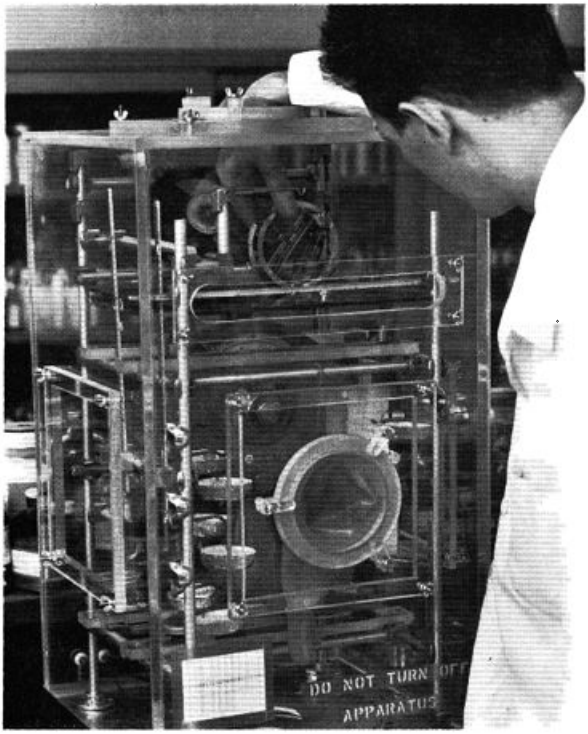

Figure 2. Chamber with Sward Hardness Rocker

PVP/VA, Nasuna A/B, shellac, and PVM/MA were tested for moisture pick-up at 70 and 90% R.H. Data for 50/50 mixtures of the above resins were also obtained. Unfortunately, this work does not include Resyn 28-1310.

Experimental

Apparatus

The Controlled Relative Humidity instrument (Model VP-100A*) was modified by replacing the original glass jar with a rectangular Plexiglass chamber (Fig. 1) which has openings for inserting rubber gloves. One additional opening in the top front side was provided for replacing the polished glass plate for Sward Hardness measurements. Because of the large size of the chamber, two additional fans were included for increasing air circulation. In the lower part of the chamber is installed a Sauter Balance† with a scale range from 0–1000 mg,

* Blue M Co., Blue Island, Ill.
† Sauter Co., Ebingen-Württ., Germany.

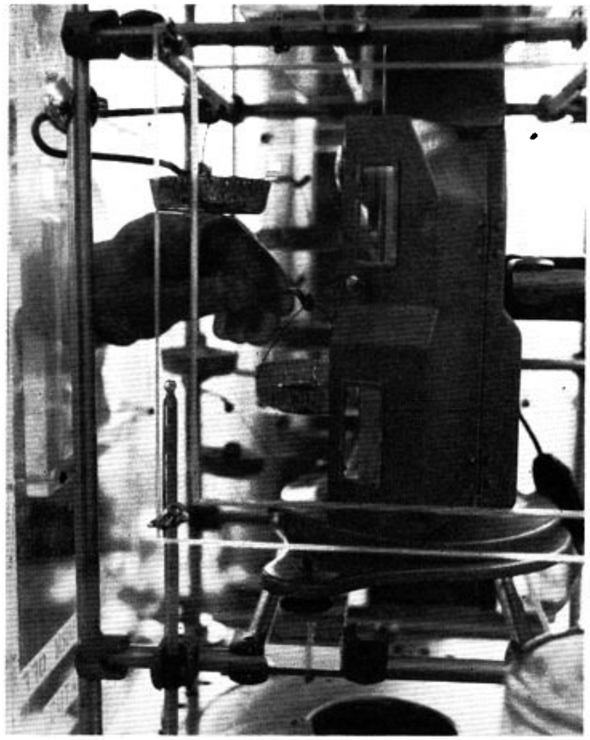

Figure 3. Sauter balance and weighing dishes

with 2 mg divisions and 1 mg sensitivity. In order to run hardness measurements simultaneously with moisture pick-up, a Sward Hardness* instrument was inserted into the top part of the chamber (Fig. 2). For cooling, tap water was used, which made it possible to adjust the relative humidity from 50% up to 90%. Lower relative humidities could have been obtained by the use of colder circulating water, but that range was of no interest in these experiments.

A constant temperature of 29.5 °C was maintained in the chamber for all tests. It was possible to control the temperature in the chamber within ±0.05 °C and the relative humidity within ±0.5%.

The usual manner of obtaining relative humidity utilizes dry and wet bulb thermometers. In general, wet bulb readings depend on the air velocities over the wet wick. At lower air velocities, higher wet bulb temperature will result, and hence a higher humidity reading will be made. By the use of a Bendix Psychron Model 566† which is de-

* Gardner Laboratory, Inc., Bethesda, Md.

† The Bendix Corp., Baltimore, Md.

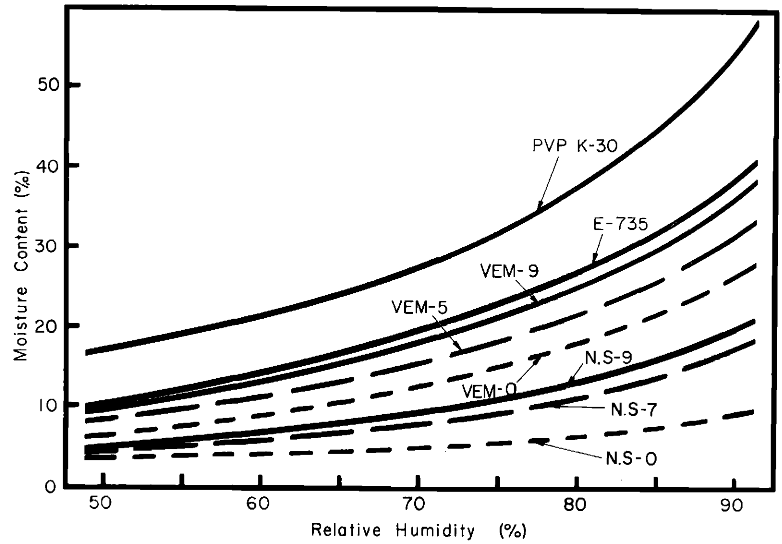

Figure 4. Moisture absorption of various resin films *vs.* relative humidity (30°C)

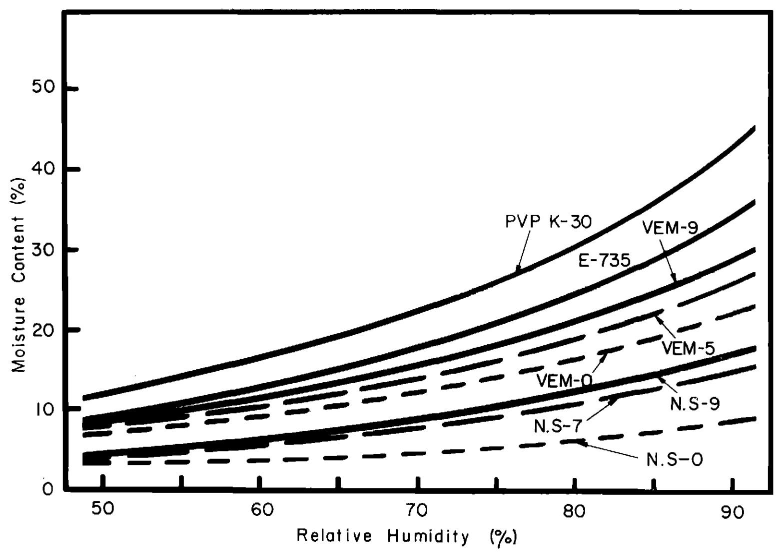

Figure 5. Moisture absorption of various films with 3.5% plasticizer (Silicone oil DC 555) *vs.* relative humidity (30°C)

signed to meet U. S. Weather Bureau specification and which uses an air velocity of 5 m/sec past the wet and dry bulb, it was found that the air velocity in the chamber was high enough to obtain correct relative humidity readings.

Method

Approximately 1.25 g of a 40% solution of resin in anhydrous ethanol was placed evenly in an aluminum dish (diameter 5.1 cm) provided with a hanger and dried at room temperature over a period of two days. At the end of this time a uniformly dried film formed on the bottom of the dish. Final drying of the film was done at 105 °C for a 2-hour period in a circulating oven. In this way it was possible to obtain a resinous film weighing 0.5 ± 0.02 g in each dish with practically no surface bubbles, which might increase the surface in contact with air and probably would change the rate of conditioning. This arrangement made it possible to place eight dishes on hangers in the chamber for one run. For the determination of moisture pick-up or loss the dishes were placed on the hook of the Sauter Balance (Fig. 3), weighed, and then returned to the hangers.

For Sward Hardness measurement three different films were cast on the polished glass plate from a 40% solution of the resin in anhydrous ethanol having a wet thickness of 3×10^{-3} in. (1.2×10^{-3} cm). These films were then dried at room temperature outside of the chamber for two days. In this way the air in the chamber was not contaminated with alcohol vapor. Then the glass plate with the films was placed in the chamber and conditioned for two days under the humidity conditions desired for determining the hardness. It was found that this time period was sufficient to obtain equilibrium conditions of the films. Duplicate hardness measurements were taken about six hours later to check the results.

Results

Data shown include results obtained with four resins commercially used as hair fixatives: National Starch Resyn 28-1310, G. Barr Co. VEM Resin, Antara PVP/VA E-735, and Antara PVP K-30. The first two resins have carboxylic groups which, for hair spray purposes, usually are neutralized with an amino-alcohol. In the case of Resyn 28-1310, 90% (N.S-9) and 70% (N.S-7) neutralization with AMPD and also unneutralized resin (N.S-0) were used. The VEM resin was 90% neutralized (VEM-9) and 50% neutralized (VEM-5) with AMPD, as

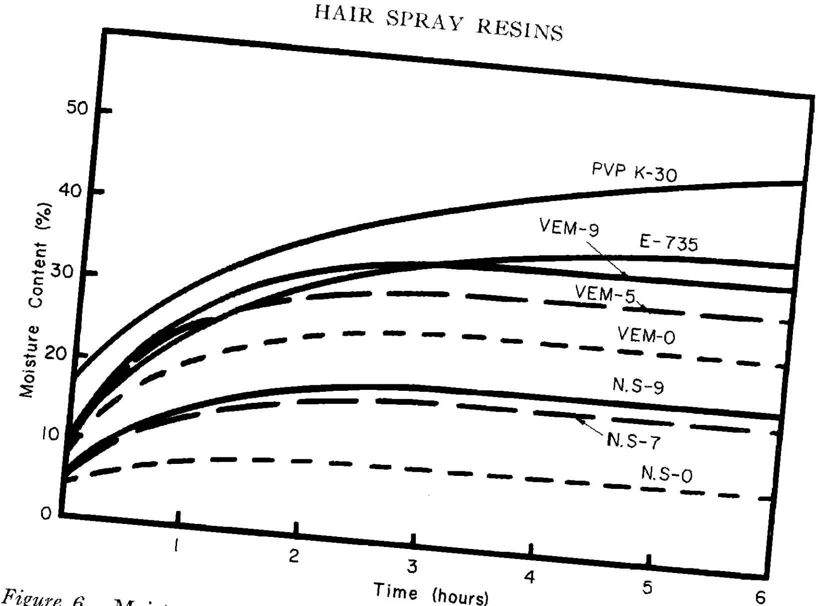

Figure 6. Moisture absorption of various resin films *vs.* time upon conditioning from 50 to 90% relative humidity (30°C)

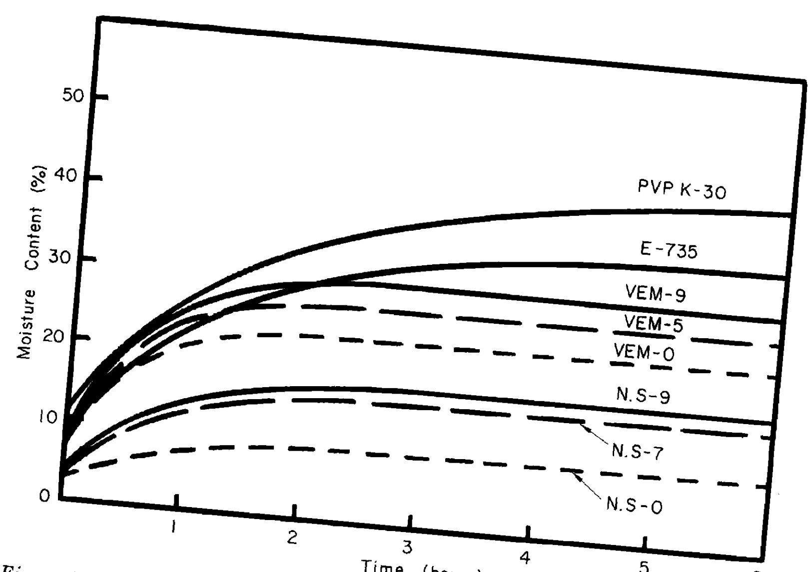

Figure 7. Moisture absorption of various resin films with 3.5% plasticizer (Silicone oil DC 555) *vs.* time upon conditioning from 50 to 90% relative humidity (30°C)

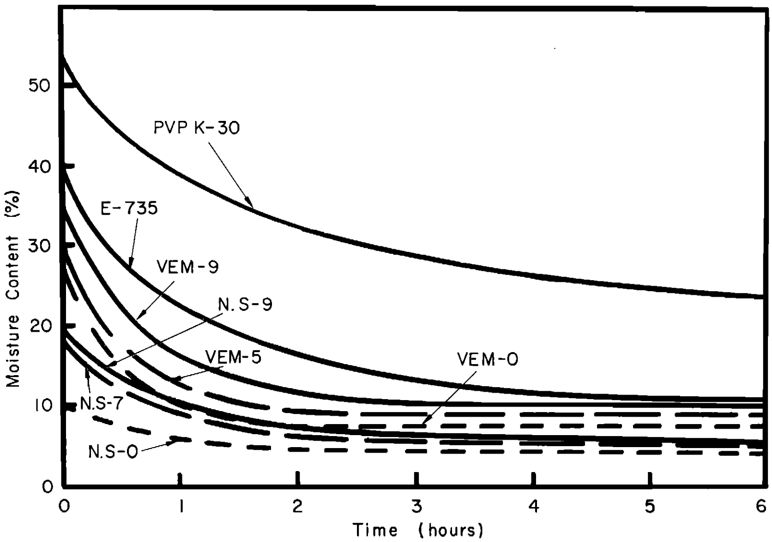

Figure 8. Drying of various resin films *vs.* time upon conditioning from 90 to 50% relative humidity (30°C)

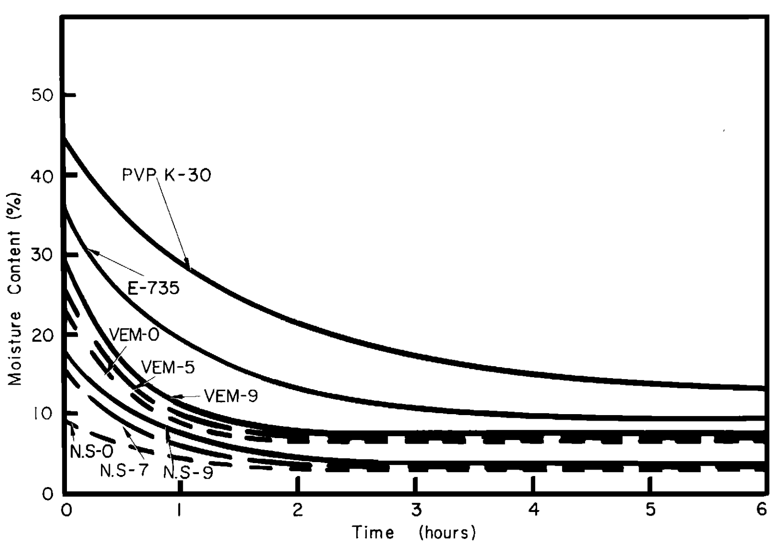

Figure 9. Drying of various resin films with 3.5% plasticizer (Silicone oil DC 555) *vs.* time upon conditioning from 90 to 50% relative humidity (30°C)

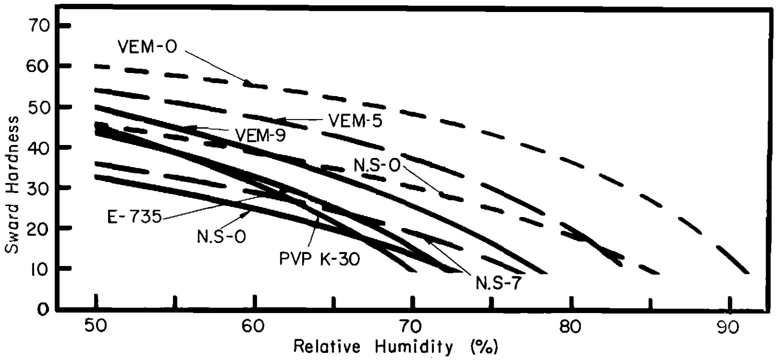

Figure 10. Sward hardness of various resin films *vs.* relative humidity (30°C)

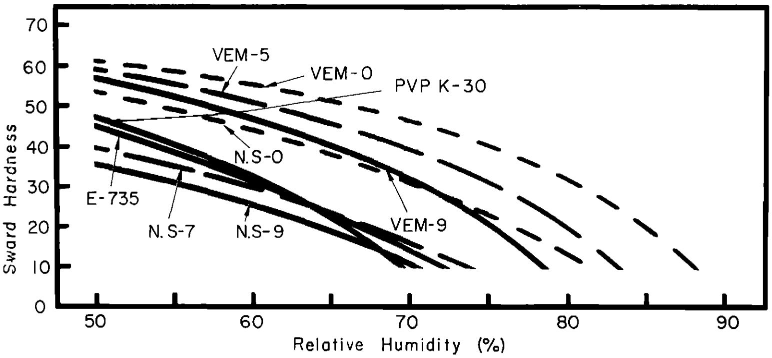

Figure 11. Sward hardness of various resin films with 3.5% plasticizer (Silicone oil DC 555) *vs.* relative humidity (30°C)

well as unneutralized (VEM-0). The percentage of water absorption is based on dry resin. All tests were made with films with and without plasticizer. Whenever a plasticizer was used, it was 3.5% Silicone Oil DC 555* based on dry resin.

Figure 4 shows the moisture absorption at different relative humidities of various resin films at equilibrium. PVP K-30 shows the greatest moisture absorption, followed by PVP/VA 735. VEM has lower humidity pick-up. As can be anticipated, unneutralized resin has lower moisture absorption than does neutralized resin because of its lower water solubility. Resyn 28-1310 has the lowest moisture absorption. Figure 5 shows the results with plasticized films. There is a decrease in the water absorption of the plasticized films in comparison with the nonplasticized films.

* Dow Corning Corp., Midland, Mich.

Figure 6 shows the moisture absorption rate of these films conditioned at 50% relative humidity and then exposed to 90% RH. Both carboxylic types of resin have a much faster conditioning rate than PVP/VA 735 and finally PVP K-30. Plasticized films have approximately the same conditioning rate (Fig. 7), except that the initial and final absorptions are lower than those of unplasticized films.

The drying rate of films conditioned at 90% RH and then exposed to 50% RH is shown in Fig. 8. Equilibrium is reached by all the films in two to four hours except PVP/VA 735 and PVP K-30. Figure 9 gives the results with films that have been plasticized. The drying rate curves of plasticized films are all displaced downward due to the hydrophobic character of the plasticizer.

Figure 10 shows the variation of Sward Hardness with relative humidities from 50 to 90% at equilibrium. It can be seen that the unneutralized VEM-0 and 50% neutralized VEM-5 give the hardest films. These are followed by 90% neutralized VEM-9, except beyond 61% RH where the hardness is surpassed by the unneutralized Resyn 28-1310. It can be seen that the hardness of both the PVP K-30 and PVP/VA 735 decrease more rapidly. Figure 11 gives similar data using plasticized films. Hardness obtained with plasticized films with silicone oil could, of course, be affected by at least three factors: (a) plasticizer decreases the moisture pick-up which results in harder film; (b) plasticizer itself decreases the hardness; and (c) plasticizer lubricates the surface between the film and the Sward Hardness rocker, thereby increasing the Sward Hardness reading. Each of these factors may produce different effects, even on the same plasticized film at different humidities.

Conclusions

In conclusion, it can be seen from the foregoing that the greater the degree of neutralization the greater the hygroscopicity of the films of carboxylic types of resins. PVP/VA 735 and PVP K-30 films are more hygroscopic than any of the films made with VEM or the Resyn 28-1310 resins. Although moisture pick-up by the VEM resin is greater than that of Resyn 28-1310, the hardness of the former at any given humidity is greater. Greater hardness at high humidity means less tack. A hard film on the hair will break more easily when the comb is passed through, whereas a soft, tacky film will put drag on the comb. Soft, tacky films will also result in hair snagging with resultant difficulty in combing. A certain degree of moisture pick-up is perhaps desirable because it makes the films more flexible and prevents flaking since the absorbed water acts like a plasticizer.

It is to be understood from the data presented that several resins are available to give any desired hygroscopicity or hardness characteristics; the data should not be construed to show relative ratings. Soft and tacky films may be desirable for such formulations in which sticking together of hair after combing is of prime importance.

(Received June 8, 1966)

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(6) Private Communication, Daikin Kyogo Co., Ltd.

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