A study of wetting tension solutions

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ABSTRACT: Within the printing and packaging industry, wetting tension solutions, prepared from mixtures of ethylene glycol monoethyl ether and formamide, are used to determine printability, coating lay down, and heat sealability of treated plastic films, especially polyethylenes and polypropylene. These solutions were studied using the method of maximum bubble pressure of surface tension measurement in order to determine the relationship between ASTM/TAPPI designated dyne numbers and actual surface tension values. In addition, the effects that age, temperature, and amount of colorant have on surface tension values of respective solutions were also examined. Results showed that measured surface tension values are lower than ASTM/TAPPI designated numbers for low numbered solutions and slightly higher for other solutions in the set. In addition, age and use tend to increase actual surface tension values of lower numbered solutions more readily than higher numbered solutions, because ethylene glycol monoethyl ether is more volatile than formamide. The amount of colorant added to the solutions does not affect surface tension values.

KEYWORDS: ASTM, ethylene glycol, formamide, mixed ethers, mixtures, plastic films, polyethylene, polypropylene, solutions, surface tension, TAPPI, wetting.

Within the printing and packaging industry, adhesion of an ink, coating, or adhesive to a polymer film, such as polyethylene (PE) or polypropylene (PP), is dependent upon the nature of the film's surface. One of the common ways to measure the relative ability of a polymer film to accept and retain inks, coatings, and adhesives is by using a series of wetting tension solutions.

Measurement of surface energies of polymer films can be performed by using solutions composed of formamide ($HCONH_2$) and ethyl Cellosolve® (ethylene glycol monoethyl ether, $CH_3CH_2OCH_2$-CH_2OH). Such wetting tension solutions are prepared by mixing the two reagents in proportions shown in **Table I** and described in ASTM and TAPPI methods *(1, 2)*. ASTM/TAPPI designated solution numbers (i.e., 30–56) are the surface tension values determined by the DuNouy method, which uses a platinum-iridium test ring *(1)*.

Visibility of drops or thin films of wetting tension solutions is increased by adding a colorant of high tinctorial value to each solution. Basic Fuchsin biological stain or Du Pont victoria pure blue BO dye are usually used as colorants.

Use of wetting tension solutions

Polymer surface wetting tension testing is performed by applying solutions of increasing wetting tension to the polymer film until a solution is found that just wets the polymer surface. The surface tension of the polymer film's surface is approximately equal to the surface tension of that particular mixture. Typically, cotton-tipped applicators are used to apply wetting tension liquids to polymer surfaces. Alternatively, full etch coating rods and solution-filled pens can be used to smoothly apply wetting tension solutions across polymer surfaces.

When a cotton applicator is used, a solution is spread lightly over an area of approximately 1 $in.^2$ (6.5 cm^2).

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I. Concentrations of ethyl Cellosolve–formamide mixtures used in making wetting tension solutions.

Formamide, vol. %	*Ethyl Cellosolve, %*	*Wetting tension[a], dynes/cm*
0	100.0	30
2.5	97.5	31
10.5	89.5	32
19.0	81.0	33
26.5	73.5	34
35.0	65.0	35
42.5	57.5	36
48.5	51.5	37
54.0	46.0	38
59.0	41.0	39
63.5	36.5	40
67.5	32.5	41
71.5	28.5	42
74.7	25.3	43
78.0	22.0	44
80.3	19.7	45
83.0	17.0	46
87.0	13.0	48
90.7	9.3	50
93.7	6.3	52
96.5	3.5	54
99.0	1.0	56

[a] Measured under conditions of 23 ± 2°C and 50 ± 5% RH.

The time required for the continuous film of liquid to break up into droplets is noted. If the continuous liquid film holds for two or more seconds, the next higher surface tension solution is tried. If the continuous liquid film breaks into droplets in less than 2 s, then the next lower numbered solution is tried. It is recommended that the analyst check wetting tensions of polymer films by working progressively to higher surface tension mixtures. This technique leads to better precision in reading surface energies, because wettability (lower solution numbers) is easier to see than marginal, nonwettability (higher solution numbers).

Known interferences to this method include polymer surface and glass storage bottle contamination. Surface-active impurities, either on the polymer surface or in the wetting tension solution, will affect results. Surfactants that are incorporated with certain polymers to change their characteristics can also affect results *(3)*. Polymer films being tested are not to be touched or rubbed. Also, if the polymer film surface has been unevenly treated, no single wetting tension value can describe it. Glass apparatus should be free of detergents, which have very strong surface tension reducing characteristics.

According to ASTM and TAPPI methods, tests should be conducted at standard conditions (23± 2°C and 50± 5% RH on polymer films conditioned for 40 h at those conditions. However, the wetting tension solution kit is often used in manufacturing plant environments that are not at "standard" temperature and humidity. In addition, samples are often tested straight off the extruder or treater and not "conditioned" prior to testing. Therefore, interested personnel should run tests at each condition on the same samples to establish a correlation factor between surface tension readings at manufacturing plant conditions and those at standard conditions.

Polymer surface treatment

Plastics, in general, have chemically inert and nonporous surfaces with low surface energies which cause them to be nonreceptive to bonding with printing inks, coatings, and adhesives. There are several polymer surface treatment techniques that can be used to improve a polymer film's ability to retain a coating, ink, or adhesive. Polymers such as PE and PP have very low surface energies (28–30 dynes/cm), and these surfaces usually have to be treated in order to improve bonding characteristics. Other polymers (e.g., polyester), foils, and paper are also surface treated. The three most common methods by which surfaces are treated are (a) flame treatment, (b) etching by means of acid or plasma, and (c) corona discharge (including ozone generation). Molded parts are often treated by flame or etching. Polymer films, once extensively treated by flame, are now almost exclusively treated by corona discharge.

Corona treatment is strictly a surface phenomenon, with the depth of penetration measured in Ångstroms. Polymer films are corona treated to improve wettability and improve the ability of inks, coatings, and adhesives to bond to surfaces *(4, 5)*. Treatments typically raise surface energies of PE and PP from 28–30 dynes/cm to greater than 35 dynes/cm. Corona treatment of polymer films is done by passing the polymer film through a capacitor which has an electrode as one plate and a grounded roller as the other capacitor plate with the combination of polymer film, roller cover, and air making up the dielectric of the capacitor. A corona is generated when ionization of the air occurs. The greater the air ionization, the higher is the level of treatment applied to the polymer's surface *(6)*.

Surface tension measurements of liquids

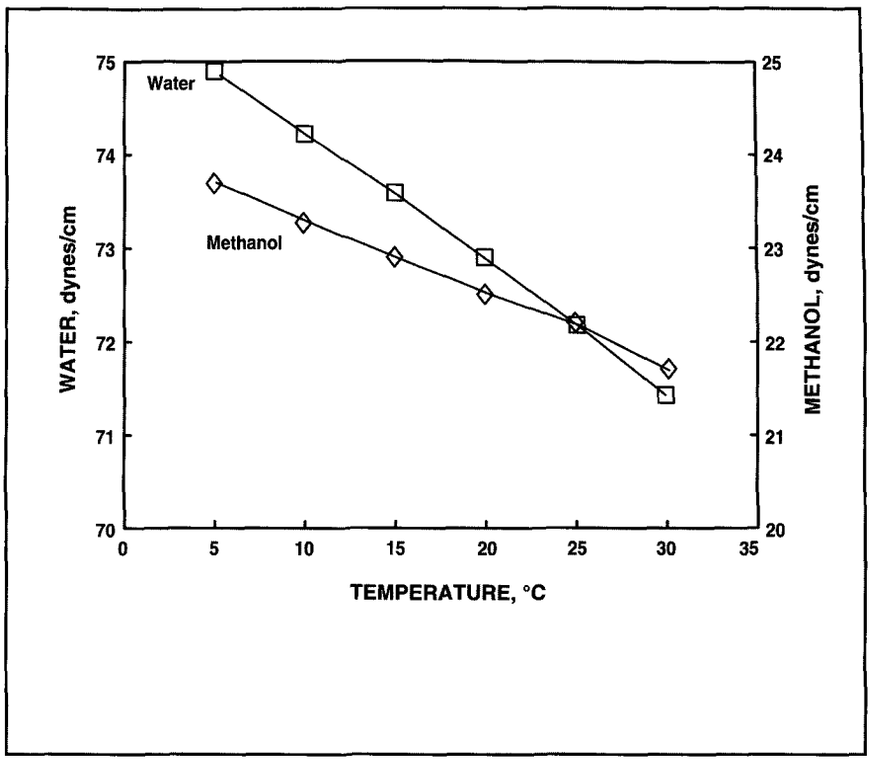
Molecules at the surface of a liquid are attracted into the body of the liquid, because the attraction of the underlying molecules is greater than the attraction by the vapor molecules on the other side of the surface. This inward attraction causes the surface to contract, if it can, and gives rise to a force in the plane of the surface. Equation 1 shows that the surface tension, ∂, of a liquid is the force, F, per unit length on the surface that opposes the expansion of the surface area, where l is the length and the factor 2 is introduced, because there are two liquid surfaces. In the established literature, surface tensions are expressed as dynes/cm although millinewton/meter is used, also.

$$\partial = F/2l \qquad (1)$$

Surface tension values of liquids can be determined in the laboratory by various methods, including the Wilhelmy plate, DuNouy ring, sessile drop, pendant drop, capillary height, drop weight, and maximum bubble pressure.

The only instrument available for continuous process measurement of surface tension is that which uses the maximum bubble pressure technique *(7–12)*. The DuNouy ring and capillary height methods require clean surfaces without surface contaminants in order to obtain accurate surface tension measurements. These latter methods, for example, cannot be used for liquids which exhibit foaming or which have surface debris. Surface tension at the topmost level of the liquid is measured by the capillary height or ring methods and this reading cannot indicate whether the liquid itself is homogeneous or heterogeneous. With the maximum bubble pressure method, surface tension measurements are taken within the bulk of the fluid; surface foam or insoluble surface contaminants do not affect surface tension readings.

1. Effect of temperature on surface tensions of standard liquids



The determination of surface tension by measurement of the pressure required to liberate bubbles from a vertical capillary tube immersed in a liquid is known as the method of maximum bubble pressure. This technique of surface tension measurement was first suggested in 1851 *(13)*, then developed and used as a comparative method *(14)* and, finally, used for the absolute determination of surface tensions of a large number of substances *(15)*. The first accurate theory of the method was given in 1892 *(16)*, modified in 1915 *(17)*, and then expanded *(18)*.

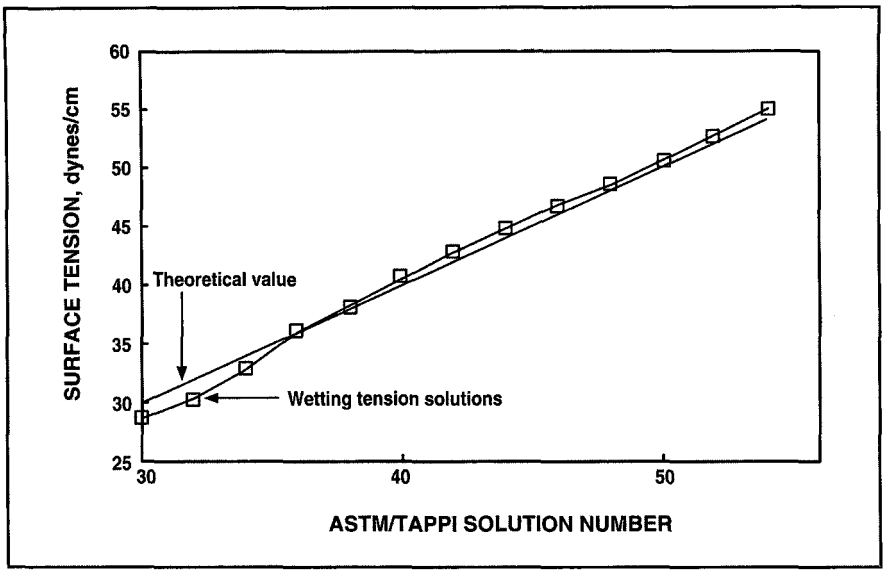
Calibration of the instrument for surface tension measurements using the maximum bubble pressure technique consists of immersing the capillary probes successively in two, known, standard fluids and adjusting instrument readings. Calibration fluids chosen are those which are pure, readily available, and do not pose hazards. Water (high surface tension; 72.9 dynes/cm at 20°C) and a low surface tension fluid (methanol, 22.5 dynes/cm at 20°C; heptane, 20.1 dynes/cm at 20°C; or isopropanol, 21.3 dynes/cm at 20°C) are usually used.

Surface tension values of liquids decrease as temperature increases, because energy added to the liquid disrupts the attractive forces between molecules of liquids that lead to surface tension. This inverse temperature-surface tension relation for water and methanol is illustrated in **Fig. 1**. Under ordinary conditions (i.e., far below the critical temperature), surface tensions of most small molecule liquids vary linearly with temperature.

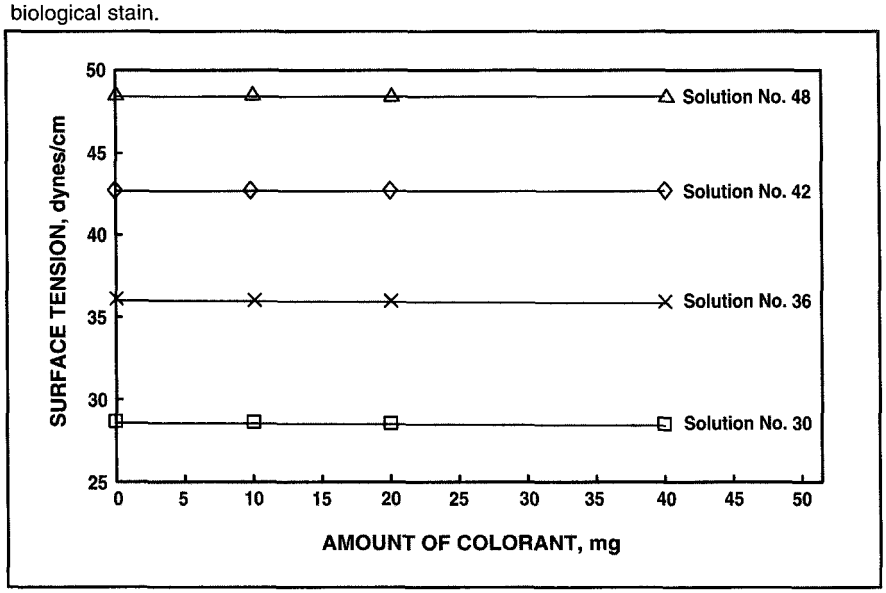
Purposes of study

The two primary purposes of this study were to (a) determine the relationship between ASTM/TAPPI wetting tension solution designated numbers (i.e., 30–56) and actual surface tension measurements using the

2. Surface tension values and ASTM/TAPPI designated numbers. Conditioned at 23°C.



3. Effect of amount of colorant on surface tension values of solutions. Basic Fuchsin biological stain.



method of maximum bubble pressure and (b) assess the effects of aging, temperature, and amount of colorant on surface tension values of wetting tension solutions.

Experimental

Three sets of wetting tension solutions were prepared from ethyl Cellosolve and formamide under different conditions. The three conditions were chosen to simulate possible conditions encountered in practical use situations. The preparation and storage conditions were as follows:

1. Prepared and stored at ASTM/TAPPI standard conditions (23 ± 2°C and 50% RH).
2. Prepared in the laboratory where the temperature varied (20–32°C) and stored at ASTM/TAPPI conditions.
3. Prepared and stored in the laboratory where the temperature varied (20-32°C).

Surface tension values and temperatures of solutions were measured using a SensaDyne Model 5000 Surface Tensiometer (Manufactured by Chem Dyne Research Corp., Mesa, AR 85275-0430). This instrument applies the method of maximum bubble pressure. The instrument was calibrated with water (high surface tension) and methanol (low surface tension). Surface tension measurements had a variability of ± 0.1 dyne/cm, while temperature measurements had a variability of ± 0.1°C. Accurate temperature measurements are vital, because of the inverse relationship between surface tension and temperature.

For those studies of the effect of colorant on surface tension values of respective solutions, Basic Fuchsin biological stain was added in 10-mg quantities via a dentist's single-end lever amalgam carrier.

Results and discussion

All three sets of wetting tension solutions showed the same characteristics when ASTM/TAPPI designated solution numbers were compared to measured surface tension values. **Figure 2** shows that wetting tension solution numbers 30–35 had measured surface tension values below ASTM/TAPPI designated numbers. Wetting tension solution numbers above 36 had measured surface tension values that were slightly higher than ASTM designated numbers. This cross-over region (36–38 dynes/cm) coincides with the region were solutions are composed of approximately equal quantities of ethyl Cellosolve and formamide. That is, between 36 dynes/cm and 38 dynes/cm, solvent and solute roles of the two liquids change. Also, since measured surface tension values for ethyl Cellosolve were lower than theoretical values (28.6 vs. 30 dynes/cm), the

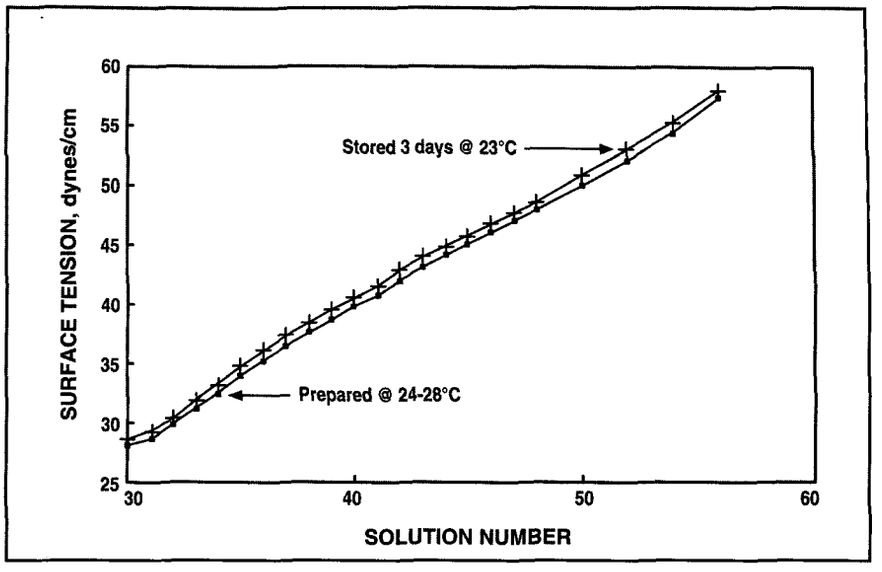
cross-over point occurs in that region where the "influence" of formamide is greater than that of ethyl Cellosolve.

It was found also that the amount of Basic Fuchsin colorant added to wetting tension solutions (up to 40 mg/50 mL of solution) has no effect on surface tensions of the solutions. This is illustrated in **Fig. 3**, which shows no changes in surfaces tensions of four respective wetting tension solutions to which Basic Fuchsin was added.

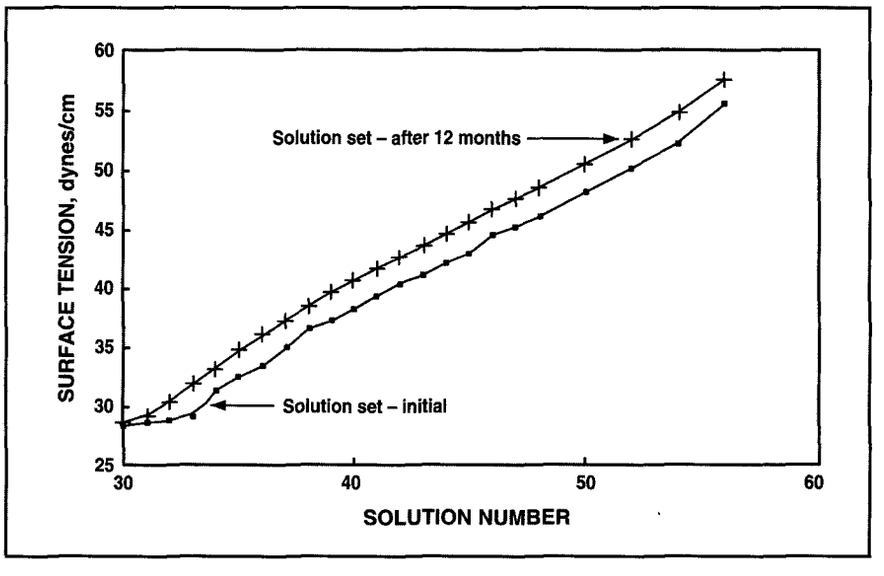
Temperature was found to have a significant effect on measured surface tension values of wetting tension solutions. **Figure 4** shows surface tension values initially obtained on a set of wetting tension solutions prepared at temperatures which ranged from 24°C to 28°C (lower curve) and surface tension values obtained on the same set of solutions after conditioning the solutions at 23°C for three days (upper curve).

Long-term storage and usage of wetting tension solutions were found to cause significant increases in respective surface tension values, as seen in **Fig. 5**. Formamide is less volatile than ethyl Cellosolve.* Since wetting tension solutions with lower numbers contain more ethyl Cellosolve than higher numbered solutions, evaporation effects should increase actual surface tension values of numbered solutions more readily than higher numbered solutions. The set of wetting tension solutions which were stored for 12 months for this study was not heavily used. A higher rate of usage would likely exacerbate this effect due to more ethyl Cellosolve evaporation.

4. Effect of temperature on surface tensions of solutions



5. Effect of long-term storage on surface tensions of solutions



Conclusions

Within the printing and packaging industry, accurate wetting tension solutions are used to determine printability, coating lay down, and adhesive bondability of treated plastic films, especially PE and PP. A set of wetting tension solutions provides a quick and convenient way to characterize a film's surface. Our study has led to the following conclusions:

With care and moderate use levels, wetting tension solutions should be usable for over a year and should give accurate wetting tension readings during their life time.

The amount of colorant added to wetting tension solutions (up to 40 mg/50 mL of solution) does not affect measured surface tension values.

Evaporation effects on improperly stored and handled solutions should increase surface tension values, because ethyl Cellosolve is more readily volatile than formamide. A

*On a scale where the very volatile ethyl ether is assigned an evaporation rate of 1.0, Cellosolve (being less volatile than ethyl ether) has a rate of 28, and the relatively non-volatile formamide has an evaporation rate > 300.

consequence of this is that PE and PP films may be judged suitable for printing when, in fact, these films cannot be printed.

Wetting tension solutions whose temperatures are higher than the standard 23± 2°C will have lower measured surface tension values, because the added energy of higher temperatures disrupts the intermolecular attractive forces which lead to surface tension.

Recommendations

The care with which a set of wetting tension solutions is handled and the extent of use will determine the accuracy that the set can read wetting tensions of polymer films. Conclusions of this study lead to the following recommendations:

1. Prepare wetting tension solutions at standard conditions to ensure accurate respective solvent concentrations in the solutions.
2. Perform wetting tension tests on polymer films at standard conditions to ensure precision in surface treatments.
3. If tests must be performed online under nonstandard conditions, develop a temperature versus wetting tension relation to ensure accuracy of surface treatment assessments.
4. Replace, periodically, wetting tension solutions that get used extensively, because evaporation and contamination may affect their accuracy. If unsure, measure surface tension values of solutions before testing. Stock solutions can be kept sealed and refrigerated for replenishing individual solutions if they go bad. The ASTM and TAPPI methods list a precision of ± 0.5 dynes/cm for an individual user of wetting tension solutions. If solutions' surface tension values deviate more than this from the ASTM/TAPPI designated numbers, solutions should be replaced.
5. Dispose of unusable solutions in a manner which complies with safety regulations.

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