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An Apparatus for the Determination of the Minimum Film Temperature of Polymer Emulsions

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I. INTRODUCTION

An apparatus has been constructed and tested which permits an easy and reproducible determination of the minimum temperature at which a polymer emulsion will deposit a continuous film. This minimum filming temperature (MFT) is one of the most important properties of any polymer emulsion which is used where the filming properties are important, such as in clear or pigmented coatings. In using a paint or a paper coating, for example, it is vitally important to obtain sufficient coalescence of the polymer emulsion particles to achieve continuity in the film and adhesion to the surface.

It may, however, be undesirable to employ polymers of extremely low MFT in order to assure formation of well coalesced films, for these polymers may concomitantly evidence softness and stickiness at temperatures of use. Thus, a strict control and knowledge of the MFT is usually desirable.

From a scientific standpoint, the process of film formation has received some attention, and mechanisms have been suggested as representing the course of film formation. Henson, Taber, and Bradford[1] have proposed the mechanism to be that of sintering of the particles, following compaction and water loss, in a process in which the polymer surface tension provides the driving force and the polymer viscosity is rate-determining.

Brown,[2] on the other hand, proposes that water evaporation from the capillaries in the surface of the partially dried emulsion is responsible for film formation. Following initial compaction of the particles into a close-packed configuration as the result of water evaporation, it is proposed that the tensile strength and adhesion to the polymer of the interstitial water cause the polymer to be "pulled" into the void spaces as the water is moved to the surface under surface tension forces. Evaporation at the surface results in a continual flow of water to the surface. Film formation is accomplished if the viscoelastic properties of the polymer permit sufficient deformation to accomplish coalescence under the driving force available.

Ideally, experimental investigation of film formation should provide further elucidation of the mechanism of film formation, allowing verification of these (or other) proposed mechanisms.

II. EXPERIMENTAL METHODS

A. Construction of Apparatus

The minimum film temperature tester consists of an aluminum slab in which a fixed temperature gradient is maintained by heating at one end and cooling at the other. The polymeric emulsion is painted in a strip along this slab; the point at which the film becomes discontinuous when dry is observed, and this temperature is recorded. The minimum film temperature apparatus is, in essence,

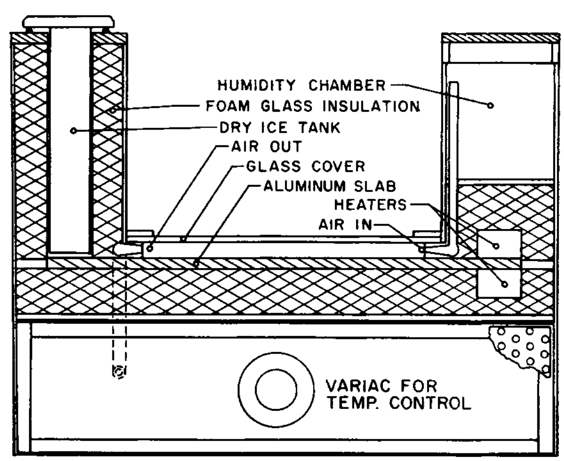

Figure 1.

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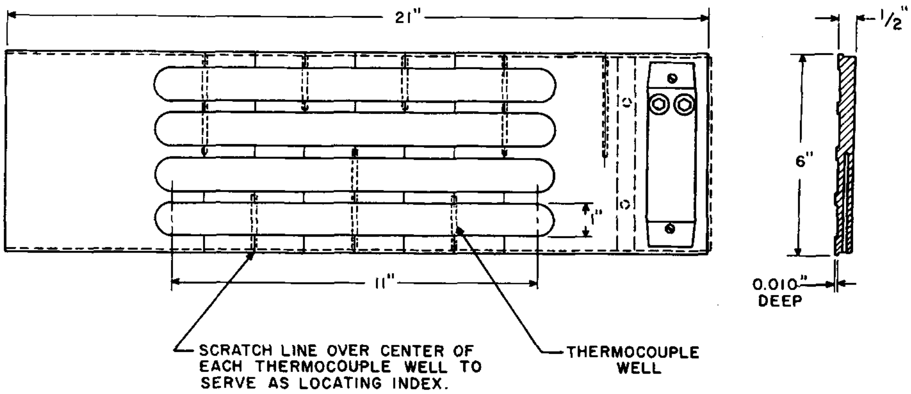

Figure 2.

a rather elaborately modified Parr bar, such as is used in melting point determinations.

The schematic diagram in Figure 1 shows a cross section of the apparatus. The aluminum plate has a Dry Ice tank mounted on one end and electrical heaters on the other. The plate is covered with a glass cover. Air of controlled humidity can be sucked or pulled across the plates through ducts at either end. The aluminum plate, heaters, and ice tank are thermally insulated with foam glass. The Variac is used to adjust the voltage applied to the heaters.

Figure 2 shows the details of the aluminum test plate. Aluminum was used for this plate because of its high thermal conductivity. An alternative would be copper; however, many emulsions contain acidic components, and corrosion problems would be severe. In the test area of the slab, four parallel depressions, about 0.010 in. deep and 1 in. wide, are milled. These serve to confine and delineate the emulsion being tested. Surface tension keeps the emulsion uniform in thickness across these test strips; consequently, drying is also uniform. Seven thermocouples are mounted in the test area of the slab with their junctions at the points indicated by the end of the thermocouple wells in Figure 2. (In the final model the thermocouple wells were drilled from the bottom of the plate rather than the side.) An eighth thermocouple is located near the heater and serves to measure or monitor the heating rate. These eight thermocouples are connected to a Honeywell multiple-point strip-chart temperature recorder. Index marks are scribed on the slab between the test strips to indicate the location of the thermocouples.

The slab is heated by two 250-w. heaters located as shown in Figure 2. These heaters are in series with a Variac which is used to control the heat input rate. The two heaters may be switched to either series or parallel operation by a toggle switch on the instrument panel, thus providing two different heat inputs.

The slab is cooled by a tank located at the end opposite the heater containing Dry Ice–acetone or ice–water mixtures. The flow of heat to this sink is controlled by adjusting the area of the tank which is in contact with the test slab. No controlling devices are used to control the heat input or cooling. Tests are carried out after a thermal equilibrium has been reached. The entire apparatus, assembled and ready for use, is shown in Figure 3.

Tests are usually run with the slab open to the air. However, where control of humidity and/or drying rate is desirable, a cover is provided. This can be conveniently accomplished in many cases simply by covering the wet emulsion sample on the slab with a piece of cellophane. The glass cover permits visual observation of the film during drying. Air can be drawn over the emulsion by the ducts at either end of the slab. The rate of drying of the emulsion film can be partially controlled by the moisture content of this air. At temperatures

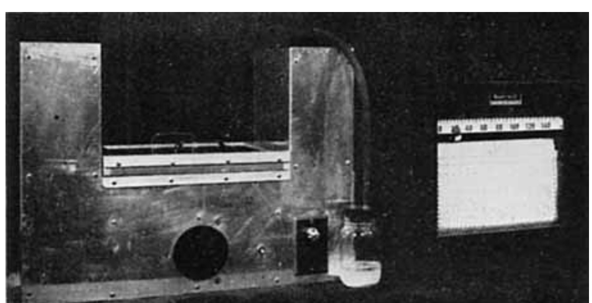

Fig. 3. Minimum film temperature apparatus.

below room temperature the air is first dried by being passed through $CaCl_2$ and a Dry Ice trap. If films are to dry at low temperatures the air must be very dry so the dew point will be below the freezing point of the aqueous phase (usually 0°C.). At temperatures above room temperature the drying rate is fast, and it is frequently desirable to slow down evaporation by saturating the air with water vapor.

B. Temperature Calibration

As the thermocouples are not located exactly at the surface of the slab, check tests were run to be certain the recorded temperatures were approximately equal to the surface temperature. The performance of each thermocouple was checked by determining the melting point of water (0°C.) and phenyl salicylate (43°C.) at each thermocouple location. Observation of the freezing point of water and dew point of air showed that the temperature was uniform across the slab.

C. Operation Range

The temperature range in the test area of the slab is controlled by varying the cooling bath and the Variac input to the heater. Typical operating conditions are listed in Table I.

TABLE I
Typical Operating Conditions for Film Temperature Tester

Temperature range in test area, °C.	Cooling bath	Heater setting	Variac setting
60–110	Ice	Low	100
51–88	Ice	Low	80
31–51	Ice	Low	54
10–55	Dry Ice–acetone	Low	72
0–35	Dry Ice-acetone	Low	66
0–30	Dry Ice–acetone	Low	55

D. Test Procedure

The test procedure used has been standardized as follows.

1. Temperature equilibrium is set up in the slab.

2. From 1 to 2 cc. of emulsion is put in the test strip with an eye dropper.

3. The emulsion is spread uniformly along the test strip with a Plexiglas spreader.

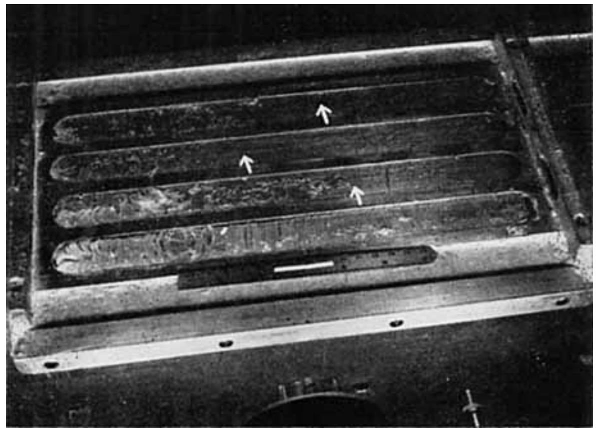

Fig. 4. Test slab showing typical films formed from polymer emulsions. Points of transition from continuous to discontinuous film indicated by arrows.

4. The glass cover may in certain cases be placed over the test slab and sealed with masking tape.

5. The emulsion is observed periodically until dry. The point at which the film becomes discontinuous is noted and recorded.

Following completion of the test, the emulsion films appear as shown in Figure 4. A reasonably sharp dividing line is evident between the area where the emulsion evaporated at temperatures insufficient for film formation and the area of continuous film formation. Below the MFT, the deposit usually is not powdery, but consists of fragmented slivers or chunks which lack clarity, continuity, and strength.

III. EXPERIMENTAL RESULTS

The apparatus has been used to measure the MFT of a number of samples for both research and product control purposes. The samples tested have represented variations in composition and in compounding. The effects of varying particle size, emulsion dilution, polymer molecular weight, etc., have been examined. The apparatus is particularly useful in the control testing of products in that it furnishes a quick index of a polymer property in a test run on its emulsion. Results from a few of the tests are reported below.

A number of tests were run on a 55/45 methyl methacrylate/ethyl acrylate (MMA/EA) nonionic emulsion of 45% solids. A variation in wet film thickness did not alter the MFT appreciably, as shown by an experiment in which the slab was left uncovered (Table II).

TABLE II

Amt. wet emulsion used, cc.	Dry film thickness, in.	MFT, °C.
1	0.004	39
2	0.004	39
4	0.011	40
8	0.018	38

The application of a relatively constant volume of emulsion, diluted to a variety of concentrations, also produced little variation in MFT (Table III).

TABLE III

Polymeric solids in emulsion, %	Dry film thickness, in.	MFT, °C.
45	0.010	39
22	0.006	39
15	0.003	39
9	0.002	38

The regular substrate in the minimum film temperature tester is aluminum. In one series of experiments the aluminum was coated with a thin, continuous, dry film of polymer from other emulsions before the experimental emulsion was tested. Results are given in Table IV.

TABLE IV

Substrate	T_i of polymeric substrate, °C.	MFT of substrate, °C.	MFT of exptl. emulsion, °C.
Aluminum	—	—	39
Polymethyl acrylate	19	1	41
Experimental 55/45 MMA/EA polymer	39	39	39

The above results indicate little influence on MFT of the substrate. However, it is observed in practice that application to porous substrates, into which the water readily penetrates, results in many cases in appreciably higher MFT values. Thus, an observation on a nonporous substrate may be regarded as the lowest value obtainable for a sample.

The drying time is influenced by such factors as film thickness, relative humidity, and temperature. In one experiment a film of the experimental emulsion was covered with a glass plate, an air gap of less than $^1/_{16}$ in. being left between the wet film

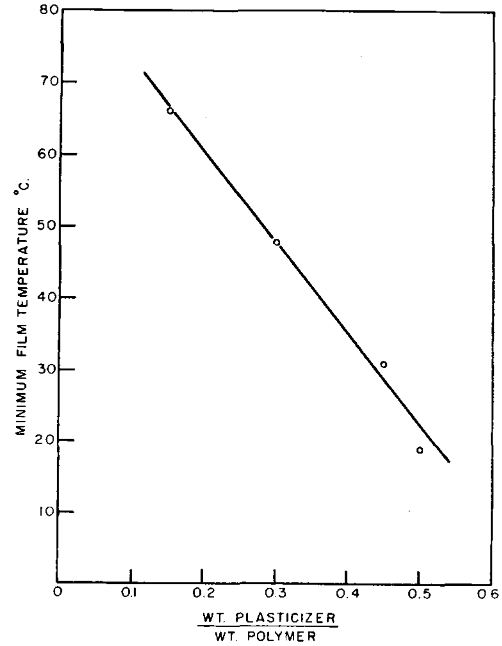

Fig. 5. Minimum film temperature of plasticized 90/10 MMA/EA polymer.

and the glass plate. This retarded the evaporation of the water from the film, which dried in 2 hr.; the MFT in this case was 35°C. A similar film,

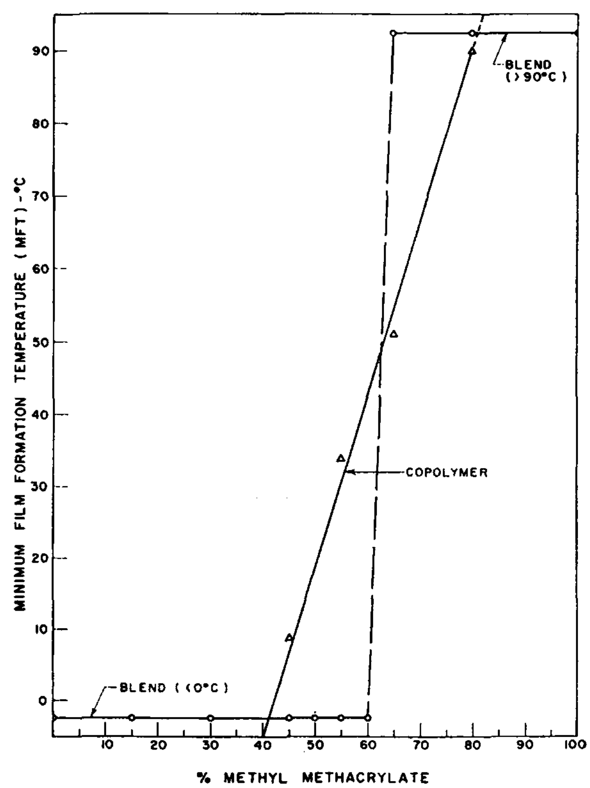

Figure 6.

exposed to ambient room air, dried in 15 min. and had an MFT of 39°C.

The effect of added plasticizers in lowering the MFT of hard polymers has been recognized and employed commercially for some time. A 90/10 methyl methacrylate/ethyl acrylate emulsion polymer with a MFT above 90°C. was modified by addition of dibutyl phthalate. The MFT values are shown graphically in Figure 5 for various ratios of plasticizer to polymer.

The effect of a systematic variation in polymer composition is shown in Figure 6. The variation was accomplished in two different ways. First, copolymers of ethyl acrylate and methyl methacrylate were prepared. The general shape of the curve is that which would be anticipated on the basis of the influence of composition on the glass temperature. Plasticization of the polymer by water and emulsifier may account for the somewhat lower values of MFT than might be predicted for the samples richest in ethyl acrylate. The second set of compositional variables is for blends of polyethyl acrylate emulsion with polymethyl methacrylate emulsion. The sharp rise in MFT here may be interpreted as resulting from purely geometrical considerations. Below a certain ratio of the emulsions, sufficient soft polymer (polyethyl acrylate) is present to bind the nondeformable polymethyl methacrylate particles. Above this critical ratio, film formation is not possible until the very high temperatures at which the harder polymer deforms are reached.

References

1. Henson, W. A., D. A. Taber, and E. B. Bradford, *Ind. Eng. Chem.*, **45**, 735 (1953).
2. Brown, G. L., *J. Polymer Sci.*, **22**, 423 (1956).

Synopsis

An apparatus has been constructed for measurement of the minimum filming temperature (MFT) of a polymer emulsion. The apparatus consists of a metal bar along which a temperature gradient may be maintained. Recessed channels are provided in which emulsion samples are spread and allowed to dry. Eight thermocouple stations along the bar are connected to a continuous recorder. Following drying of the film, the minimum temperature at which a continuous film is formed is determined. Testing of the apparatus on one emulsion examined under a variety of conditions and on samples of varying composition has demonstrated the reliability, versatility, and utility of the apparatus.

Résumé

On a construit un appareil pour la mesure de la température minimum de formation de film (MFT) d'une émulsion de polymère. L'appareil se compose d'une barre métallique au long de laquelle on maintient un gradient de température. On adjoint des canaux renforcés dans lesquels les échantillons d émulsion sont répandus et y peuvent y sècher. Huit thermocouples situés le long de la barre sont reliés à un enregistreur continu. Suite au sèchage du film, on détermine la température minimale à laquelle se forme un film continu. Le contrôle de l'appareil avec und émulsion examinée sous diverses conditions et avec des échantillons de composition variable ont montré que l'appareil pouvait donner des mesures exactes, varieés et utiles.

Zusammenfassung

Ein Apparat zur Messung des Temperaturminimums für Filmbildung (MFT) einer Polymeremulsion wurde konstruiert. Der Apparat besteht aus einem Metallstab, entlang welchem ein Temperaturgradient aufrecht erhalten wird. Es sind vertiefte Kanäle vorgesehen, welche die Emulsionsproben aufnehmen und in denen diese zur Trocknung gebracht werden. Acht längs des Stabes verteilte Thermoelemente sind mit einem kontinuierlichen Rekorder verbunden. Nach dem Trocknen der Filme, wird das Temperaturminimum bestimmt, bei dem noch ein kontinuierlicher Film entsteht. Bestimmungen, die mit dem Apparat an einer Emulsion unter verschiedenen Bedingungen und an Proben verscheidener Zusammensetzung vorgenommen wurden, bewiesen seine Verlässlichkeit, Brauchbarkeit und weite Anwendbarkeit

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