TIGRES
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Industrial quality test at the cleaning of adhesion areas

Measurement of the surface energy with test inks

Measurement of the surface energy of cleaned surfaces

The effect of the cleaning by rinsing or by plasma-treatment can be measured by expensive methods in the laboratory. However, a wetting test with test inks is often sufficient for an industrial quality check. The methods of these tests are described in this paper.

1. Background

Fat and oil reject liquids. It is commonly known, that this water rejecting effect is used to prevent corrosion of metallic surfaces by oiling these parts. However, these oil films also prevent adhesion of lacquers and glues, so that a cleaning or degreasing is necessary before coating or gluing. Polymers behave themselves to liquids like oils. These materials must be modified on the surface, in order to increase wetting and adhesion. Independent of materials in question, cleaning and treatment methods and also of subsequent coating processes, the question of a simple and reproducible measurement and quantification of the surface state arises in industry.

Whether a liquid, for instance a glue, wets a surface or not, depends on the liquid in question, as well as on the material, with which the liquid comes in contact on the surface. YOUNG's equation describes the dependence of the wetting angle on the surface energies of the three involved surfaces.

YOUNG's equation:

$$\cos \theta = (\sigma_s - \sigma_{sl} - \pi_e) / \sigma_l = \sigma_c / \sigma_l$$

with

θ	=	contact angle
σ_s	=	surface energy of the solid work piece
σ_{sl}	=	energy of the interface substrate - glue
σ_l	=	surface energy of the liquid glue

The contact angle is the angle that the surface of a liquid droplet forms with solid surfaces at the contact point. The droplet runs off the surface, if the contact angle exceeds 90°: the substrate is oily or fatty. The droplet sits on the surface at angles between 90° and 0°: the liquid wets the surface. The liquid runs on the surface at a contact angle of 0°: the liquid spreads on the surface. For instance, water spreads on clean metallic surfaces. Spreading of water makes a high demand on pretreatment of polymeric plastics, however, is not necessary in most cases, since the surface energy of water based colour systems is not as high as pure water. Surface energy σ_s quantifies the wettability of a material. The surface energy of metallic surfaces is a measure of the quality of a cleaning process, since the contamination on metal surfaces consists almost of oil and fat.

The main difficulty of the application of YOUNG's equation results from the impossibility to determine the boundary energy σ_{sl} in a direct experiment, so that measurements of the contact angle cannot be evaluated in a direct way. In order to obtain a practically applicable equation, that contains only experimentally accessible parameters, a „critical surface energy" σ_c of the substrate is introduced:

$$\sigma_s - \sigma_{sl} = \sigma_c$$

This critical surface energy σ_c can be determined experimentally by putting a drop of a liquid with a known surface energy σ_l onto the substrate and by measuring the angle θ with a microscope or by a shadow method. If looked precisely, the value of surface energy that is determined in this way, however, is valid only for the liquid used or for similar liquids, since σ_{sl} depends on the chemical nature of the liquids.

Measuring edge angles is at one side too expensive for daily routine work and on the other side only spot measurements can be performed. In order to have besides this laboratory method a safe method for the measurement in the production, film producing industry has developed some simple and quick methods, which can also be used for the quality check of the degreasing of metallic parts. In general, no information is obtained about type and origin of a contamination with the wetting tests described in this paper. This is reserved to intense physical or chemical methods. However, wetting tests give safe information whether a cleaning of a metal or a pretreatment of a plastic is performed properly.

Was the surface energy of Aluminium casted parts determined to 30 mN/m, for instance, the surface is contaminated with Polyethylene from the demounting agent, which exhibits normally a surface energy in this range. These PE-residuals lead to disturbances at the lacquering process or during the application of a liquid sealing. Surface energies below approx. 25 mN/m indicate a silicon-organic contamination. A metallic surface is clean, if it becomes wetted by water (72 mN/m).

2. Test inks

Different series of test inks are used in the industry. The test inks are mixtures of chemicals, the production of which must be performed very carefully. Persons, who work with test inks, should know the necessary careful handling of chemicals from their professional education or experience. The potential danger at proper handling is small; especially since only small amounts of test inks are used for the measurement. To reduce endangering of one's health, the special security hints of the label and of the security manual must be followed in any case.

For storage of test inks only the general rules of the storage of chemicals have to be obeyed. Test inks are often stored in a fridge in industry, if they are not in use for longer times. There is no objection against this, if the fridge is not used also for food. A warming-up of the ink or of the samples seems not to be necessary, since the dependence on temperature of the surface energy of approx. 0,5 mN/m per 10° should be negligible in most cases.

Non-usable rests of inks, for instance from the blue series, are chemical waste, which must be disposed according to local official regulations. In order to ensure proper disposal and at high ink consumption, the author recommends to contact local waste disposal companies or to buy test inks from a supplier, who takes inks back after usage.

The blue test inks made of formamide and ethylenglycole are mostly used. They are recommended by DIN ISO 8296 as well as by ASTM D 2578-84. A series of test inks between 30 and 58 mN/m in steps of 1 mN/m is possible with the formamide-ethylenglycole mixture, the composition, however, must be kept precisely. Since both components may injure you health, pregnant women should not work with them.

The red series of water–methanol test inks is prescribed by DIN ISO 8296 for the measurement of PVC. Values from 23 to 72 mN/m are possible with this series. Due to the high volatility of methanol, the handling of inks with low values is difficult. An analogous series using a mixture of water and ethanol substitutes more and more the standard blue ink series. However, it must be carefully checked, whether the substrate or any contamination reacts with the ink.

Beside both series of DIN ISO 8296 several more series exist, which are used in special cases only. Here should be mentioned:
* Alcane-series from 16 up to 45 mN/m (polarity = 0),
* Formamide-water from 58 up to 72 mN/m (as a supplement of the blue series) and
* Water–sodium chloride from 72 up to 82 mN/m (for realisation of high surface energies).

The test liquids of the alcane-series are also used for the examination of oil-rejecting properties of refined textiles according AATCC 118-1972.

3. Measurement methods

The measurement of the (critical) surface energy depends on the subjective judgement of the wetting of a series of test liquids on the substrate to be examined. All methods mentioned here can be performed with any series of test inks. Results are reproducible within a series and are used for classification of the wetting behaviour of surfaces. Results of these tests can only be compared very restricted among each other or with results of edge angle measurements. Examined values of surface energy must only be cited together with the measurement method and the type of test ink used. You must pay attention that no chemical reaction occurs between test ink and contamination or substrate.

Ink application in stripes: former DIN 53 364

With the brush, which is mounted in the cap of each supplied test ink bottle, a 100 mm long liquid stroke must be drawn crosswise to the running direction of the web. The surface energy of the film is the value of that ink the edge of which stays stable for 2 seconds at 90 % of the stroke's length. This method determines the average (critical) surface energy. Small disturbances cannot be determined, since the ink is relatively thick and is applied only on a small area. A reproducibility of ±0.5 mN/m can be obtained with little training. Commercial sets of test inks are commercially offered in steps of 2 mN/m, since a reproducibility of ±1 mN/m is sufficient for most applications.

The main source of error of this measuring method originates from the contact of the brush on the surface to be examined. Friction, that may occur, changes the surface energy of substrates and leads also to a small contamination of the testing liquid when the brush is dipped again into the ink bottle. In order to keep the disturbance due to contaminations low, it is recommended to use only one third of the test ink bottle, respectively to change the inks after three months of usage. Due to quick and safe handling of the stripe-wise application of test inks according DIN 53 364, this method has become the standard measuring method in printing and converting industry for determination of surface energies. The length of the strokes is shortened in industrial application, if smaller work pieces must be measured.

The picture shows the traces of test inks on a plastic plate. The trace of the 30 mN/m-ink has been widened out at the edge, while the 34 mN/m-ink shrinks very fast. Precise measurements reveal a surface energy of 31 mN/m at this sample.

Areal application of test inks: DIN ISO 8296 and ASTM D 2578-84

The test ink must be applied using a cotton-wool or – much more reproducible – using a rakel or applicator on an area of approximately 50x50 mm^2 size. The surface energy is the lowest value of that ink, which forms a closed layer for at least 2 seconds. Changes at the edge are out of consideration. This method regularly reveals smaller values than DIN 53 364,since also minor inhomogeneities are included in the examination.

If an applicator is used in contrast to the ASTM-standard, a homogeneous ink application is guaranteed and reproducibility becomes clearly improved. Friction on substrates surface and contamination of the ink, which contains as natural product 5-8 % humidity, are avoided. The ink is taken from the bottle by a pipette, so that contamination is also avoided. Often, film producer and converter, who are printing or lacquering the substrate in the whole area, use this method. The areal method is not suitable for smaller work pieces.

Running droplet method: AFCO-recommendation C

The disadvantage of both methods DIN 53 364 and ASTM D 2578-84 is that contact time of ink with the substrate to be measured is sometimes too long. During this contact time, additives can migrate from plastics into the ink or the plastic may solve the ink, so that the result of the measurement gets distorted. Important printing substrates at which this occurs with formamide-ethylenglycol-inks are PVC, PU and Aluminium-foils, if a layer of rolling oil is on its surface.

Different test ink-droplets of a constant volume drop from a constant height onto the substrate, which exhibits an inclination of 40-60° at the running droplet method. The value of the test ink, which runs off without leaving a trace is a measure of the wettability of the substrate. Smaller inhomogeneities of the film surface are neglected with this method, similar to DIN 53 364. The possibilities of chemical reactions or solutions are reduced, due to small contact time. Also, no friction occurs and test inks don't become contaminated. AFCO-recommendation C is seldom applied, mostly by Aluminium producing companies.

Total dipping

A special case is the testing of water wetting by dipping. Hereby the running off of water from completely dipped parts is examined. This method, however, is only used for testing of the cleanness of metallic parts, due to the big amount of testing liquid which is necessary and due to the fact, that metals exhibits a surface energy of more than 72 mN/m when clean. The method detects also small inhomogenities. However, assessment of wetting in drilling holes and at edges of workpieces may be difficult.

Felt tip like test pens

In order to simplify the wetting test, felt tip pens filled with the known testing liquids are offered. These pens should be used very carefully. They may be helpful as a coarse control method, but should not be used as a measuring method. A reproducible measuring in the sense or DIN ISO 8296 seems only be possible in special cases. When using the pens, pay attention to the contamination of the tip by abrasion from the surface to be examined.

4. COMPARISON AND CONCLUSION

To control wetting behaviour of surfaces of different working pieces for many industrial applications, the (critical) surface energy can be examined by different wetting tests using test inks. Due to simple handling and a reproducibility of ± 0,5 mN/m, the method according the older DIN 53 364 is widely used. The modified method according ASTM D 2578-84 allows also the detection of smaller inhomogeneities.

Commercial (blue) formamide-ethylenglycol-test inks are widely used, since they are proven for most industrial applications. Beside these, also other series of test inks are offered, which may be used in special cases or for internal examinations. Among these, the ethanol-water series has to be mentioned, since these liquids are harmless to human health.

All herein described measuring methods are non-contact-less and destroy measured surfaces, since the inks contaminate the surfaces. A contact-less method to determine the thickness of layers on metallic surfaces is for instance the ellipsometric method, which works also at high speeds in the sub-µm-region.

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