

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

Wavelock Advanced Technology Co., Ltd.,
Petitioner

v.

Textron Innovations Inc.
Patent Owner

Patent No. 6,455,138
Issue Date: September 24, 2002
Title: METALLIZED SHEETING, COMPOSITES,
AND METHODS FOR THEIR FORMATION

Inter Partes Review No. IPR2013-00149 (SCM)

SECOND DECLARATION OF ROBERT IEZZI, Ph.D.

I. INTRODUCTION

1. I have been retained by Morrison & Foerster LLP in this case as an expert in the relevant art.

2. I am the same Robert Iezzi who previously provided a first declaration in support of the Petition For *Inter Partes* Review for U.S. Patent No. 6,455,138 dated February 14, 2013.

3. I submit this Second Declaration in support of Petitioner Wavelock Advanced Technology Co., LTD's Reply to Patent Owner's Response.

4. In addition to the materials I reviewed when preparing my first declaration, I have reviewed Patent Owner's Corrected Response dated October 9, 2013 (Paper 16) ("Response").

5. As discussed in my first declaration, a person of ordinary skill in the art relevant to the '138 patent would have had at least a bachelor's degree in chemical engineering, material science, or chemistry, and at least five years of experience working with or researching thermoplastic films and composites. The statements in this declaration of what one of ordinary skill in the art would have known or understood are based on the filing date of the '138 patent, i.e., December 31, 1997.

6. I have been informed and understand the description of a claim element in a prior art reference can be express or inherent. For a prior art reference

to describe a claim element inherently, the claim element must be necessarily present. Probabilities are not sufficient to establish inherency.

7. In its Response, Patent Owner challenges my finding that the discrete islands of Kuwahara are in adhesive. My finding was based on numerous facts in Kuwahara as understood by one of ordinary skill in the art. Patent Owner seeks to cast doubt on some of these facts. After reviewing the Response, I disagree with Patent Owner's arguments. My opinions and underlying reasoning for the opinions in response to Patent Owner are set forth below. To the extent that I refer to printed publications in the accompanying appendices, I have no reason to doubt that the printed publications were published on the dates indicated on the printed publications.

II. THE ADHESIVE OF KUWAHARA IS A LIQUID

8. In the Response, Patent Owner contends that I erroneously understood the adhesive to be a liquid based on Kuwahara's disclosure that the adhesive was applied by roll coating. (Response at pp. 22-23.) In my opinion, a person of ordinary skill in the art would have understood Kuwahara's express disclosure of the roll coated adhesive to refer to a liquid adhesive. This opinion is consistent with how Patent Owner's Ex. 2002 describes roll coating. For example, the first two sentences of Ex. 2002 provide: "Roll coating machines are commonly used for the application of *a liquid* to the surface of a part. Rollcoaters can be used to

apply *liquid adhesives*, paints, oils, and coatings such as varnish or clear finish coats.” (Ex. 2002 at p. 1 (emphasis added).) Ex. 2002 further states: “The type of *adhesive* or coating will influence the way the *liquids* are brought to the metering point.” (*Id.* at p. 10 (emphasis added).) There is no mention at all in Ex. 2002 of non-liquids being applied by roll coaters.

9. In addition, Kuwahara expressly discloses the adhesive as vinyl chloride-vinyl acetate copolymer adhesive. (Kuwahara at 5:14-27.) Persons of ordinary skill in the art would have understood that this adhesive is applied as a liquid. The *Adhesives Technology Handbook* at pages 127-128 states: “PVC and copolymers of both *vinyl chloride and vinyl acetate* with other monomers, such as maleic acid esters, alkyl acrylates, maleic anhydride, and ethylene, are also used to produce solvent-based adhesives.” (Ebnesajjad, S., *Adhesives Technology Handbook*, 2nd ed., 2008 (emphasis added) (App. AA).) Solvent based adhesives are clearly liquids. Further, Skeist’s *Handbook of Adhesives* at page 280 teaches: “*Vinyl dispersion* resins have typically consisted of inert homopolymer or copolymers of vinyl chloride and vinyl acetate....” (Skeist, I., *Handbook of Adhesives*, 3rd ed., 1990 (emphasis added) (App. BB).) Persons of ordinary skilled in the art of adhesives would have known that a vinyl chloride-vinyl acetate *dispersion* is a liquid.

10. Based on Kuwahara's express disclosure of roll coating adhesive and as further confirmed by Patent Owner's Ex. 2002 and the above references describing a vinyl chloride-vinyl acetate copolymer adhesive as a liquid, one of ordinary skill in the art would have necessarily understood Kuwahara's adhesive as a liquid.

11. In the Response, Patent Owner points to the electrostatic printing process of Xerox machines as an example of roll coating a solid. (Response at p. 21.) One of ordinary skill in the art would not have considered electrostatic printing using charged toner particles roll coating, and thus would not have understood Kuwahara's reference to roll coating in the manner asserted by Patent Owner. This argument is also inconsistent with Patent Owner's Ex. 2002, which states: "A roll coating machine works by transferring a layer of coating from the surface of a roller to the surface of a part. When this happens, a phenomenon known as 'film splitting' occurs. The layer of coating on the surface of the roll splits – part of it stays on the roller, and part sticks to the surface of the part. The percentage of coating that sticks to the part (the substrate) depends on the surface characteristics of both the roller and the substrate." That is, roll coating relies on a liquid's adhesive properties to itself, to the surfaces of the roller and to the application surface. In comparison, Xerox machines transfer particles from a

charged toner drum to paper using electrostatic charge—there is no film splitting in a Xerox machine.

III. THE LIQUID ADHESIVE WOULD FLOW INTO THE VOIDS IN KUWAHARA'S METALLIZED LAYER

12. In the Response, Patent Owner states that Kuwahara discloses spaces between islands of 500 Angstroms. (Response at p. 24.) However, Kuwahara explicitly discloses distances between islands of up to 5000 Angstroms. Specifically, Kuwahara at 4:6-7 states: “The distance between the islands is set to between 100 and 5000 Å.” Given this express disclosure of 5000 Angstroms, persons of ordinary skill in the art would not have understood Kuwahara as limited to 500 Angstroms spacings. Instead, persons of ordinary skill in the art would have understood that the vinyl chloride-vinyl acetate adhesive of Examples 1 and 2 would have flowed around areas between islands with spacings of 500 Angstroms or up to 5000 Angstroms.

1. The viscosity of the adhesive in Kuwahara was low enough to flow between the islands

13. Persons of ordinary skill in the art would have understood that the viscosity of the vinyl chloride-vinyl acetate adhesive in Kuwahara was applied with a low enough viscosity to flow between the metal islands in Examples 1 and 2.

14. Patent Owner contends that the copolymer resin could be so viscous that it would not flow and “fill” any voids. (*See, e.g.*, Response at p. 24.) This argument is inconsistent with Kuwahara’s express disclosure of roll coating an adhesive. Roll coating, as Patent Owner’s Ex. 2002 explains, is a method of applying a liquid film layer. Highly viscous liquids cannot be rolled coated as they would form clumps or bind up the equipment. As Ex. 2002 states: “Certain types of adhesives (such as hotmelts, waxes and *certain high viscosity materials*) require that the machine or the rollers be heated *to melt the material or lower the viscosity to a point where it can be applied.*” (Ex. 2002 at p. 10 (emphasis added).)

15. In addition, Kuwahara states that the “vinyl chloride-vinyl acetate copolymer resin was applied to the deposited Sn layer of the examples to a thickness of 2 μ m with a roller coater, then *heated* with a 2002 μ m thick polyvinylchloride film and *laminated under pressure.*” (Ex. 1007 at 5:19-22 (emphasis added).) Persons of ordinary skill in the art would have understood that the purpose of applying heat and pressure during the lamination process is to get the adhesive to flow in order to obtain intimate contact between the adhesive and surface features of the surfaces being laminated in order to create the laminated article. Accordingly, persons of ordinary skill in the art would have understood that the vinyl chloride-vinyl acetate adhesive in Kuwahara would have further necessarily flowed between the metal islands in Examples 1 and 2 when heat and

pressure was applied during the lamination process. Thus, Patent Owner's argument as to highly viscous liquids fails to take into account how one of ordinary skill in the art would have understood Kuwahara's express disclosure of roll coating adhesive and then lamination with heat and pressure.

2. The diameter of the polymer molecules of the adhesive in Kuwahara would be below 500 Angstroms

16. In the Response, Patent Owner argues that the discrete islands could not be in the Kuwahara adhesive because the molecular weight, and hence the length of the polymer chains, of the vinyl chloride-vinyl acetate adhesive are too large to physically fit in the 500 Angstroms spacing between the discrete islands. (Response at p. 25.) I disagree. Persons of ordinary skill in the art would have understood that it is the polymer diameter and mobility, and not the polymer length, that determine whether a polymer would flow between the spacing between the discrete islands. As described below, persons of ordinary skill in the art would have understood that the polymer diameter was well below 500 Angstroms and, therefore, necessarily would have flowed between the metal islands in Examples 1 and 2 of Kuwahara.

17. Typical polymer molecules are very thin and flexible like cooked spaghetti. In a flowing adhesive, the huge number of polymer chains would be

oriented in every conceivable direction. The chains that are aligned width-wise with the openings would necessarily flow between the metal islands.

18. This result is confirmed when the calculations are applied specifically to a vinyl chloride-vinyl acetate adhesive as disclosed in Kuwahara. Zang, Y.-H. *et al.* at pages 1965-68 provide the cross-sectional area of poly-vinyl-chloride and poly-vinyl-acetate polymers. (Zang, Y.-H and Carreau, P. J., *A Correlation Between Critical End-to-End Distance for Entanglements and Molecular Chain Diameter of Polymers*, J. Appl. Polym. Sci. (1991), 42: 1965–1968 (App. CC).) This reference explains that the polymer chain diameter can be estimated by taking the square root of these areas. (*Id.* at 1965.) The cross-sectional area of poly-vinyl-chloride is 27.2 square Angstroms. (*Id.* at 1966.) Taking the square root of 27.2 square Angstroms gives us an estimated average polymer diameter of 5.2 Angstroms for poly-vinyl-chloride. Similarly, the cross-sectional area of poly-vinyl-acetate is 59.3 square Angstroms. (*See id.*) Taking the square root of 59.3 square Angstroms gives us an estimated average polymer diameter of 7.7 Angstroms for poly-vinyl-acetate. Even assuming that these polymer chains appear exactly side by side in a vinyl chloride-vinyl acetate adhesive, the total polymer chain diameter would be 12.9 Angstroms, considerably below both the 5000 and 500 Angstrom spacing between the discrete islands disclosed in Kuwahara.

IV. KUWAHARA'S ROLLER COATS THE LIQUID RESIN ONTO THE METALLIZED LAYER

19. In the Response, the Patent Owner states that I am “implying that a liquid is applied to the top of the metallized film as it might be oriented vertically, and consequently, gravity would cause the liquid to seep into the spaces between the islands of metal.” (Response at pp. 27-28.) I disagree with this characterization of my first declaration. The term “top” in my first declaration was used relative to the structure in which metal islands are formed on Kuwahara’s PET layer. This term was not meant to identify any positioning with respect to coordinates external to the structure.

20. One of ordinary skill in the art would not have understood Kuwahara as requiring gravity to force the vinyl chloride-vinyl acetate adhesive between the metal islands. Adhesives can be applied “upside down” by roll coating because the driving forces, such as (a) surface tension; (b) capillary action; (c) the adhesive’s polymer chain small molecular diameter, mobility, and orientation; and (d) intrinsic molecular inter-diffusion, cause the adhesive to spread into the crevices of a surface and obtain intimate contact with the surface.

21. A liquid adhesive “wets” the solid surface it comes into contact with and spreads across all exposed surfaces (including the exposed surfaces between

the islands). Wetting is the ability of a liquid to maintain contact with a contact surface due to intermolecular interactions.

22. It is well-known to one skilled in the art of adhesive and coatings technology that for a liquid to wet a solid surface, the surface tension of the liquid must be lower than the surface tension of the solid, and that metals have a high surface tension relative to adhesives and are easily coated by polymer adhesives and coatings. This is reinforced by Wicks at p. 125: “The surface tension of a clean metal surface (usually, metal oxide) is higher than that of any potential coating.” (Wicks, Z.W., Jr., et. al., *Organic Coatings Science & Technology*, 3rd ed., 2007 (App. DD).)

23. The surface tension of tin metal islands in Kuwahara is 587 dyne/cm calculated as follows.

$\sigma (T) = 570.0 - 0.08 (T - T_m)^1$ where σ is mN/m; T is °K; T_m is tin melt temperature = 505°K

σ at room temperature (20°C = 293°K) = 570.0 – 0.08 (293°K - 505°K)

$\sigma = 587$ mN/m

1 mN/m = 1 dyne/cm ^{Footnote 2}

¹ Alchagirov, B.B., et al., *Surface Tension of Tin and Its Alloys with Lead*, Russian Journal of Physical Chemistry A, vol. 81, no. 8, 2007 at p. 1281 (App. EE).

$$\sigma = 587 \text{ dyne/cm}$$

24. The surface tension of vinyl chloride is 41.9 dyne/cm, and of vinyl acetate is 36.5 dyne/cm. (Baghdachi, J.A., *Fundamentals of Adhesion*, J. of Coatings Technology, vol. 69, no. 870, July, 1997, at p. 90 (App. FF).) Thus, the vinyl chloride-vinyl acetate adhesive of Kuwahara will readily wet and flow into the metal islands.

25. The Response at page 14 also offers a scenario where solvent may be used to dissolve the resin. Typical solvents used for adhesives have much lower surface tension (about half) than the vinyl chloride-vinyl acetate adhesive, as shown in the following table:

Solvent	Surface Tension dynes/cm
Water	72.7
Ethylene glycol	48.4
Propylene glycol	36.0
o-Xylene	30.0
Toluene	28.4
n-Butyl acetate	25.2
n-Butanol	24.6
Mineral spirits	24.0
Methyl isobutyl ketone	23.6
Methanol	23.6
VM&P naphtha	22.0
n-Octane	21.8
Lactol spirits	19.9
n-Hexane	18.4

² Wicks, Z.W., Jr., et al., *Organic Coatings Science & Technology*, 3rd ed., 2007, at p. 490 (App. DD).

(Baghdachi, J.A., *Fundamentals of Adhesion*, J. of Coatings Technology, vol. 69, no. 870, July, 1997, at p. 90 (App. FF)). Therefore, if the adhesive of Kuwahara was dissolved in solvent, the surface tension of the adhesive-solvent mixture would be even lower and interact with the metal islands and flow into the spaces between the metal islands even more.

26. Capillary forces will also facilitate the flow of the adhesive into the small space between the metal islands. The *Concise Encyclopedia of Plastics* at page 134 defines capillary forces as “[t]he attraction between molecules, similar to *surface tension*, which results in the rise of a liquid in small tubes or fibers, as can occur in filled compounds or reinforced plastics.” (Rosato, D.V., et. al., *Concise Encyclopedia of Plastics*, 2000 (App. GG) (emphasis added).) The Response’s depiction of the Kuwahara’s adhesive possibly being applied to the bottom side of the part being coated is irrelevant because the adhesive will flow upwards into the small space between the metal islands due to capillary forces alone, irrespective of other driving forces such as: (a) surface tension; (b) the adhesive’s polymer chain small molecular diameter, mobility, and orientation; (c) intrinsic molecular inter-diffusion; and (d) surface roughness of the metal islands.

27. Finally, after applying the adhesive to the metal island layer, and stacking a polyvinylchloride film on top of the adhesive, Kuwahara discloses applying heat and pressure to the structure to form a lamination. (Ex. 1007 at 5:21-

22.) The heat and pressure applied during the lamination procedure would necessarily further drive the adhesive into any unfilled spaces between the islands.

V. KUWAHARA DOES NOT TEACH AWAY

28. Patent Owner argues that Kuwahara teaches away from the presence of adhesive between the islands because residual solvent would permit electricity to flow between the metal islands, which is to be avoided in Kuwahara. (Response at pp. 30-31.) This argument is incorrect since if the adhesive was conducting as the Patent Owner states, it would still electrically connect the metal islands even if it was on top of the metal islands, as the Patent Owner argues. In addition, it is known that most of the solvent would have evaporated during the lamination process. One skilled in the art would understand that the small amount of solvent that remained would not have turned a non-conducting polymer adhesive into a conductor as Patent Owner argues.

VI. CONCLUSION

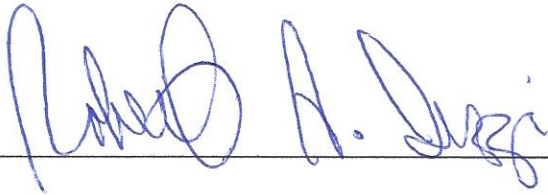
29. Patent Owner contends that my finding that the discrete islands of Kuwahara would have been in adhesive as “unsupported opinion testimony.” I disagree. As discussed in my first declaration, my finding was based on the express disclosure of Kuwahara, including references to roll coating, the spacing between the islands and the discussion of lamination by heat and pressure as understood by one of ordinary skill in the art.

30. Patent Owner's Response does not compel me to change my finding.

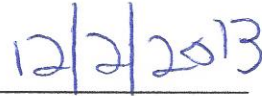
In this second declaration, I have sought to respond to Patent Owner by showing that one skilled in the art would have understood that the metal islands in Kuwahara are necessarily in adhesive for the following reasons: 1) the adhesive is roll coated as a liquid and would, therefore, have a viscosity low enough to be a mobile liquid; 2) the diameter of the adhesive polymer molecules is significantly less than the 500 Angstroms voids used in the examples of Kuwahara and even more significantly less than the 5000 Angstroms voids also disclosed in Kuwahara; 3) the "wetting" action of the adhesive and capillary action would pull the adhesive into these relatively large pores; and 4) the heat and pressure applied during the lamination procedure would further drive the adhesive into any unfilled spaces between the islands. In short, the arguments that Patent Owner has made do not properly reflect how one of ordinary skill in the art would have understood Kuwahara's facts.

31. This declaration is based on my present assessment of materials and information currently available to me. My investigation and assessment may continue, which may include reviewing documents and other information that may yet to be made available to me. Accordingly, I expressly reserve the right to continue my study in connection with this case and to expand or modify my opinions and conclusions as my study continues.

32. I declare under penalty of perjury under the laws of the United States that the foregoing is true and correct.

A handwritten signature in blue ink, appearing to read "Robert A. Iezzi", is written over a horizontal line.

Robert Iezzi

A handwritten date "12/2/2013" in blue ink is written over a horizontal line.

Date

Appendix List for Second Declaration of Robert Iezzi, Ph.D. (Exhibit 1018)**In Inter Partes Review of U.S. Patent No. 6,455,138**

Appendix Description	
Ebnesajjad, S., <i>Adhesives Technology Handbook</i> , 2 nd ed., 2008	AA
Skeist, I., <i>Handbook of Adhesives</i> , 3 rd ed., 1990	BB
Zang, Y.-H and Carreau, P. J., <i>A Correlation Between Critical End-to-End Distance for Entanglements and Molecular Chain Diameter of Polymers</i> , J. Appl. Polym. Sci. (1991), 42: 1965–1968	CC
Wicks, Z.W., Jr., et. al., <i>Organic Coatings Science & Technology</i> , 3 rd ed., 2007	DD
Alchagirov, B.B., et al., <i>Surface Tension of Tin and Its Alloys with Lead</i> , <i>Russian Journal of Physical Chemistry A</i> , vol. 81, no. 8, 2007	EE
Baghdachi, J.A., <i>Fundamentals of Adhesion</i> , J. of Coatings Technology, vol. 69, no. 870, July, 1997	FF
Rosato, D.V., et. al., <i>Concise Encyclopedia of Plastics</i> , 2000	GG



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Curing of polyvinyl butyral-phenolic film requires a temperature of 150°C at 0.10–0.20 MPa pressure. Polyvinyl formal-phenolic film, the most common form, retains adequate strength when exposed to weather, mold growth, salt spray, humidity, and chemical agents such as water, oils, and aromatic fuels. These adhesives generally have good resistance to creep, although temperatures up to 90°C produce creep and softening of some formulations. Fatigue resistance is excellent, with failure generally occurring in the adherends rather than in the adhesive, which has a service temperature range of –60°C to 100°C.^[6]

5.57 Polyvinyl Formal-Phenolics

These structural adhesives are used in bonding metal to metal in aircraft assemblies, metal honeycomb panels, and wood-to-metal sandwich construction. Other applications include bonding cyclized rubber and, in some cases, vulcanized and unvulcanized rubbers and copper foil to plastic laminates for printed circuits. They are also applied as a primer for metal-to-wood bonding with resorcinol or phenolic adhesives. Polyvinyl formal-phenolics are among the best thermosetting adhesives for metal-honeycomb and wood-metal structures. These adhesives are generally equivalent to nitrile-phenolics for strength, but have slightly better self-filleting properties for honeycomb assembly. They are superior to epoxy types where strength in sandwich construction is desirable.^[6]

5.58 Polyvinyl Butyral-Phenolics

These are used in bonding metal or reinforced plastic facings to paper (resin impregnated) honeycomb structures, cork and rubber compositions, cyclized and unvulcanized rubbers, steel to vulcanized rubber, and electrical applications. They are also used as primer for metals to be bonded to wood with phenolics. Polyvinyl butyral-phenolics lack the shear strength and toughness of the polyvinyl formal-phenolic type.^[6]

5.59 Vinyl-Resin Adhesives

Several vinyl monomers are used to prepare thermoplastics that are useful in certain adhesive applications. The most important vinyl resins for adhesives are polyvinyl acetate, polyvinyl acetals (butyral and formal), and polyvinyl alkyl ethers. PVC and copolymers of both vinyl chloride

and vinyl acetate with other monomers, such as maleic acid esters, alkyl acrylates, maleic anhydride, and ethylene, are also used to produce solvent-based adhesives.^[1]

5.60 Water-Based Adhesives

These adhesives are made from materials that can be dispersed or dissolved only in water. Some of these materials are the basis of solvent-based adhesives and are the principal materials used for liquid-adhesive formulations given in Table 5.11.

Table 5.10 lists polymers used for both water- and solvent-based adhesives. Water-based adhesives cost less than the equivalent solvent-based compounds. Even inexpensive organic solvents are costly when compared to water. The use of water eliminates problems of flammability, emission, and toxicity associated with organic solvents. However, in most cases, water-based adhesives must be kept from freezing during shipment and storage because of possible permanent damage to both the container and the contents.^[18]

There are two general types of water-based adhesives: solutions and latexes.^[96] Solutions are made from materials that are soluble only in water or in alkaline water. Examples of materials that are soluble only in water include animal glue, starch, dextrin, blood albumen, methyl cellulose, and polyvinyl alcohol. Examples of materials that are soluble in alkaline water include casein, rosin, shellac, copolymers of vinyl acetate or acrylates containing carboxyl groups, and carboxymethyl cellulose.

Latex is a stable dispersion of a polymeric material in an essentially aqueous medium. An *emulsion* is a stable dispersion of two or more immiscible

Table 5.11 Principal Polymers Used Exclusively for Water-Based Adhesives^[18]

Starch and dextrin	Casein
Gums	Sodium carboxymethylcellulose
Glue (animal)	Lignin
Albumen	Polyvinyl alcohol
Sodium silicate	

liquids held in suspension by surfactants. In the adhesives industry, natural and artificial latexes are used interchangeably. Natural latexes are obtained from the rubber tree. Synthetic latexes are obtained by emulsion polymerization of styrene, butadiene-styrene, butadiene-methacrylate, vinyl chloride, styrene-methacrylate, and styrene-butadiene. Latexes are made by dispersing particles of reclaimed rubber, butyl rubber, tar, and a large number of synthetic resins in petroleum.^[97]

Latex adhesives replace solvent-based adhesives. Most latex adhesives are specifically designed for use as adhesives. They are applied in order to obtain the proper bond. Application methods for latex adhesives include curtain coat, flow, and knife coat. Application techniques for latex adhesives are similar to those used for solvent-based adhesives. The most popular techniques are popular:^[93,96]

- *Wet bonding:* Used when the substrate is porous. The adhesive is applied to the surface. Bonding takes place while the adhesive is still wet.
- *Open-time bonding:* In this method, both surfaces are prepared and the adhesive is applied to both surfaces and allowed to dry. Bonding is achieved. At least one surface must be porous.
- *Contact bonding:* In this method, both surfaces are prepared and the adhesive is applied to one surface. Within a given time, the adhesive on the other surface near ultimate bond strength is achieved. This method, both surfaces must be porous. Latex adhesives are commonly used for contact bonding.
- *Solvent reactivation:* In this method, the adhesive is applied to the surface of the part to be bonded. The adhesive is allowed to dry. Then, by placing the part in a solvent, the adhesive is reactivated. The surface of the adhesive tacking is achieved. This method is used for small parts.

HANDBOOK OF ADHESIVES

Third Edition

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polymer for adhesion of composite structures may be obtained by balancing polymer performance in relation to water sensitivity and the substrate to be used. Metal substrates are best bonded with the medium range (15% AA) carboxyl polymers while nonpolar materials should be bonded with low AA (3%) polymers.

Hot-melt adhesives for packaging applications have been formulated using carboxyl polymers in combination with many other materials. A discussion of the properties of ethylene-ethyl acrylate (EEA) copolymers as raw materials for heat sealing and thermoplastic adhesives was presented by Kirckner in 1969.⁸⁸ The patent literature is replete with claims concerning the formulation, use, and properties of hot-melt adhesives containing a variety of carboxyl copolymers.⁸⁹⁻⁹² Guiman⁹³ reported that thermoadhesive films have been made by the radiochemical grafting of high density polyethylene with acrylic acid. Two additional patents^{94,95} described the coextrusion of nylon, carboxyl olefin, and polyethylene to produce a self-supporting multilayer film having a nominal thickness of only 1 mil. These laminates which are useful in packaging, have high strength, toughness, and clarity, excellent sealability, and firm bonding between the layers.

The development of high strength thermoplastic adhesive copolymers of the EEA type containing reactive carboxyl groups has made it practical to bond insulation such as polyethylene to metal conductors to provide adequate bonding and long term environmental resistance. Frequently, the EEA copolymer is extruded around the cable. Peacock⁹⁰ reports that when a layer of acrylic acid-ethylene copolymer (7:43) was extruded at 140°C over a flexible aluminum conductor followed by a layer of polyethylene insulation, the bond strength between the insulation and the conductor was 72 N/cm compared with 1.4 N/cm for a control assembly without the copolymer adhesive. There are numerous similar patent claims for insulated conductor cable.^{97,100}

CARBOXYL FUNCTIONAL VINYL COPOLYMER RESINS IN ADHESIVE APPLICATIONS

The incorporation of small amounts of maleic anhydride or maleic acid into copolymers of vi-

nyl chloride and vinyl acetate substantially improves their adhesion. The typical range of compositions of commercial products, such as Vinylite VMCH is 85-88 : 11: 1-3 vinyl chloride-vinyl acetate-maleic anhydride. Applications for these terpolymers include heat sealing of packaging films and vinyl plastisols with improved adhesion to substrates.¹⁰¹⁻¹⁰³

Vinyl dispersion resins have typically consisted of inert homopolymer or copolymers of vinyl chloride and vinyl acetate, and although the inertness has been of importance for a multitude of applications, there are occasions when reactive functionality is an aid. An example of such a reactive vinyl resin is Geon 137, a carboxyl modified dispersion resin with a carboxyl content equivalent to 1.79% on a resin weight basis or an acid equivalent weight of about 2500.¹⁰⁴ One adhesive application of considerable interest is in the production of flocked product, notably wall and floor coverings. A 50% replacement of standard copolymer dispersion resin with carboxyl functional resin doubles the force required to pluck fibers loose. Test results of laminating carboxylic vinyl plastisol with nylon fabric have shown a three-fold increase in adhesion.¹⁰⁴ Such plastisols also show improved adhesion to glass and polyester fabrics.¹⁰⁵

Strong durable bonds can be formed between metals and vinyl chloride polymers by using a polymeric adhesive which contains carboxyl groups and a phenol formaldehyde resin.¹⁰⁶

Plasticized PVC and vinyl chloride-vinyl acetate copolymers can be wiped with solutions of adipic, maleic, citric, and other acids, giving improved adhesion when bonding with hot-melt polyester adhesives.²⁸

CARBOXYLIC FUNCTIONAL NEOPRENES AS CONTACT ADHESIVES

Smith⁷⁷ has described in detail the practical advantages of carboxyl functional Neoprenes AF and AJ for making improved contact adhesives. The early room temperature bond strength of conventional neoprene contact adhesive is dependent on the crystallization rate of the polymer. Single component adhesive systems based on carboxyl functionality undergo crosslinking reactions with divalent

A Correlation between Critical End-to-End Distance for Entanglements and Molecular Chain Diameter of Polymers

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SYNOPSIS

The critical molecular weight M_c of 36 flexible and semirigid polymers has been studied. A unique correlation between the critical end-to-end distance $\langle R_c \rangle$ for entanglements and the average polymer chain diameter D is found. This correlation is discussed in the light of the reptation concept.

INTRODUCTION

The onset of entanglement behavior with increasing molecular weight appears universally in polymer melts and concentrated solutions.^{1,2} An example of this is the critical molecular weight M_c , which separates the dependence of zero-shear viscosity η_0 on molecular weight M into two regions: $\eta_0 \propto M$ and $\eta_0 \propto M^{3.4}$. In order to understand the molecular nature of entanglements, many attempts have been made to correlate M_c (or the critical number of main-chain bonds N_c) with some structural parameters of polymers.³⁻¹¹ A comparison of these different correlations reveals that the critical molecular weight M_c , or N_c , depends especially on the rigidity and cross-sectional area S of polymer chains. On the other hand, it has been recently recognized that entanglements can be modeled as a tube constraint on the diffusion of molecules (reptation models).^{12,13} According to the reptation models, the parameter controlling the degree of chain entanglement is the tube diameter, which is taken to be equal to the end-to-end distance between entanglements. However, no relationship between the tube diameter and the properties of polymer chains has been given. In the present work, the critical molecular weight for entanglements has been studied using the framework of the reptation models. Without linking directly M_c (or N_c) with structural parameters of polymers,

the critical end-to-end distance of a macromolecular chain for entanglements, $\langle R_c \rangle$ (corresponding to M_c), has been correlated with the average diameter D of the polymer chains.

DATA ANALYSIS

The critical end-to-end distance for entanglements, $\langle R_c \rangle$, has been calculated from the critical molecular weight M_c through the following relation¹⁴:

$$\langle R_c \rangle = \langle R_c^2 \rangle^{1/2} = M_c^{1/2} (\langle R^2 \rangle_0 / M)^{1/2} \quad (1)$$

where $\langle R^2 \rangle_0$ is the mean-square end-to-end distance for a polymer of molecular weight M in a theta solvent, which is approximately identical with that in amorphous or molten polymers.¹⁵

The use of eq. (1) implies the assumption that M_c is large enough so that the polymer chain is Gaussian.

The average polymer chain diameter D is estimated from the cross-sectional area of the polymer S using the approximate relation⁶

$$D = S^{1/2} \quad (2)$$

where the values of S are generally obtained from crystallographic data.¹⁷

Table I summarizes the values (taken from the literature) of $M_c (\langle R^2 \rangle_0 / M)^{1/2}$ and S together with the characteristic ratio C_∞ ($C_\infty = \langle R^2 \rangle_0 / Nl_0^2$, with N and l_0 being, respectively, the number and the

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Table I Critical Molecular Weight M_c and Characteristic Parameters of Polymers

No.	Polymer	M_c	C_∞	$(\langle R^2 \rangle_0/M)^{1/2}$ (Å)	S (Å ²)	$\langle R_c \rangle/D$
1	Polyethylene	3800 ^{8,18}	7.0	1.08 ¹⁶	18.3 ¹¹	15.6
2	Polypropylene	7000 ⁸	6.2	0.83 ¹⁶	34.3 ¹¹	11.9
3	Polystyrene	35,000 ^{8,18}	10.3	0.67 ¹⁶	69.8 ¹¹	15.1
4	Poly(vinyl chloride)	6250 ^{10,18}	7.7	0.82 ¹⁶	27.2 ¹¹	12.4
5	Poly(vinyl acetate)	24,500 ^{8,18}	9.0	0.70 ¹⁶	59.3 ¹¹	14.2
6	Poly(vinyl alcohol)	5300 ¹⁸	8.3	0.95 ¹⁶	21.4 ¹⁷	13.6
7	Polyacrylamide	9100 ¹⁰	14.8	1.00 ¹⁶	45.2 ¹¹	14.2
8	Poly(α -methyl styrene)	40,800 ^{5,10}	10.5	0.65 ¹⁶	100.0 ¹¹	13.1
9	Polyisobutylene	15,200 ⁸	6.2	0.74 ¹⁶	41.2 ¹¹	14.2
10	Poly(methyl acrylate)	24,100 ^{10,a}	8.0	0.68 ¹⁶	59.3 ¹¹	13.7
11	Poly(ethyl acrylate)	31,300 ^{10,a}	8.8	0.72 ¹⁶	73.0 ¹¹	14.9
12	Poly(methyl methacrylate)	31,000 ^{8,10}	8.7	0.62 ¹⁶	63.8 ¹¹	13.7
13	Poly(<i>n</i> -butyl methacrylate)	60,400 ^{10,a}	8.0	0.52 ¹⁶	93.6 ¹¹	13.2
14	Poly(<i>n</i> -hexyl methacrylate)	91,900 ^{10,a}	10.3	0.54 ¹⁶	114.2 ¹¹	15.3
15	Poly(<i>n</i> -octyl methacrylate)	114,000 ^{10,a}	10.0	0.50 ¹⁶	135.1 ¹¹	14.5
16	Poly(2-ethylbutyl methacrylate)	42,800 ^{10,a}	9.1	0.51 ¹⁶	100.0 ¹¹	10.6
17	Poly(dimethyl siloxane)	24,500 ^{8,10}	5.2	0.66 ¹⁶	63.8 ¹¹	15.6
18	Poly(ethylene oxide)	4400 ^{7,10}	4.2	0.81 ¹⁶	21.5 ¹¹	11.6
19	Poly(propylene oxide)	7700 ^{10,18}	5.1	0.77 ¹⁶	24.5 ¹¹	13.7
20	Poly(tetramethylene oxide)	2500 ¹⁰	6.1	0.93 ¹⁶	17.6 ¹⁷	11.2
21	<i>Cis</i> -polyisoprene	7700 ¹⁰	5.0	0.84 ¹⁶	28.0 ¹¹	13.9
22	Hydrogenated polyisoprene	4000 ^{10,a}	6.8 ⁸	0.92 ^b	28.5 ¹¹	11.4
23	<i>Cis, trans</i> , vinyl-polybutadiene	4500 ^{8,10}	5.4	1.01 ¹⁶	19.3 ¹¹	15.4
24	<i>Cis</i> -polybutadiene	5900 ¹⁰	4.9	0.88 ¹⁶	20.7 ¹¹	14.9
25	1,2-Polybutadiene	12,700 ^{19,a}	6.6 ⁸	0.76 ^b	49.9 ¹¹	13.7
26	Hydrogenated 1,2-polybutadiene	26,700 ^{19,a}	5.5 ¹⁹	0.68 ^b	49.9 ^c	15.8
27	Poly(ϵ -caprolactam) nylon 6	5000 ¹⁰	5.3	0.94 ¹⁶	17.9 ¹¹	15.7
28	Poly(hexamethylene adipamide) nylon 66	4700 ¹⁰	6.1	0.94 ¹⁶	17.6 ¹¹	15.4
29	Poly(decamethylene succinate)	4600 ^{10,18}	5.5 ^d	0.87 ²⁰	18.5 ^e	13.7
30	Poly(decamethylene adipate)	4400 ^{10,18}	4.8 ^d	0.83 ²⁰	18.5 ⁷	12.8
31	Poly(decamethylene sebacate)	4500 ^{10,18}	6.0 ^d	0.94 ²⁰	18.5 ⁷	14.7
32	Poly(diethylene adipate)	4800 ¹⁸	4.7 ^d	0.79 ²⁰	18.1 ¹⁷	12.9
33	Poly(ethylene terephthalate)	3300 ¹⁰		0.98 ^{16,21}	20.0 ¹¹	12.6
34	Poly(carbonate of bisphenol A)	4900 ¹⁰		0.93 ¹⁶	30.9 ¹¹	11.7
35	Poly(ester carbonate of 1- bisphenol A and 2- terephthalic acid)	4800 ¹⁰		0.95 ^f	30.9 ¹¹	11.8
36	Poly(ester of bisphenol A and diphenyl sulfone)	7100 ¹⁰		0.80 ²²	30.9 ¹¹	12.1
	Average value					13.6
	Standard deviation					0.11

^a Estimated as $M_c = 2M_e$.^b Calculated from C_∞ .^c Estimated from 1,2-polybutadiene.^d Calculated from $(\langle R^2 \rangle_0/M)$.^e Estimated from poly(decamethylene adipate) and poly(decamethylene sebacate).^f Estimated between poly(ethylene terephthalate) and poly(carbonate of bisphenol A).

average length of main-chain bonds¹⁴) for 36 polymers.

Figure 1 shows the critical end-to-end distance for entanglements $\langle R_c \rangle$ plotted as a function of D

for all of the polymers listed in Table I. Despite some scatter, $\langle R_c \rangle$ is clearly a linear function of polymer chain diameter D , given by

$$\langle R_c \rangle = 13.6D \quad (3)$$

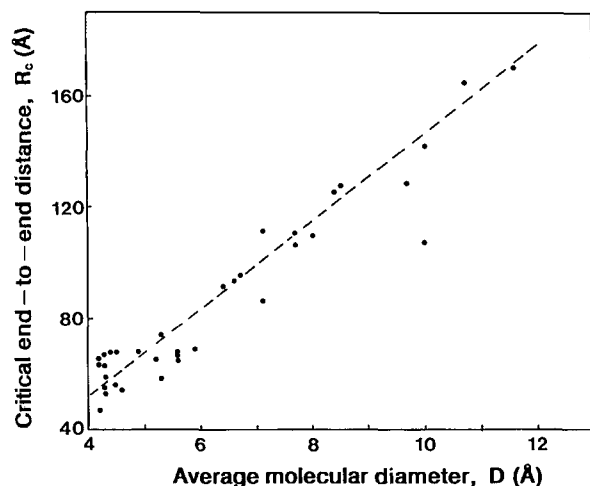


Figure 1 Critical end-to-end distance $\langle R_c \rangle$ vs. average molecular diameter D of polymer chains.

DISCUSSION AND CONCLUSION

Equation (3) provides a new correlation for entanglements relating the critical end-to-end distance to polymer chain diameter. As already mentioned in the Introduction, many other empirical correlations³⁻¹¹ have been developed before. Some similarities can be found between the proposed correlation and the literature ones: Using the relation $\langle R_c^2 \rangle = C_\infty N_c l_0^2$, the critical number of main-chain bonds N_c can be calculated from eq. (3):

$$N_c = (185/l_0^2)(D/C_\infty^{1/2})^2 \quad (4)$$

Equation (4) is similar to the Privalko-Lipatov relation,⁶ $N_c = 240 (D/\sigma)^{2.5}$, where σ is the chain stiffness factor. Moreover, Boyer and Miller⁷ pointed out that the exponent of the Privalko-Lipatov correlation should be between 2 and 2.2 instead of 2.5, thus supporting the proposed correlation.

Equation (4) predicts that for polymers with similar characteristic ratios C_∞ , like polyalkyl methacrylates, N_c should depend only on the polymer chain diameter D , or cross-sectional area S , as suggested by Boyer and Miller⁷ earlier. On the other hand, for polymers having similar average molecular diameters, N_c should decrease with increasing rigidity of the chains. This was indeed observed by Prevorsek and De Bona,²³ who reported that replacing a fraction of the flexible carbonate moiety in polycarbonates with a more rigid group (such as terephthalate) reduces the average molecular weight between entanglements.

The proposed correlation [eq. (3)] can also be reduced to a form which is similar to the Graessley-Edwards⁸ and Fox-Allen³ correlations for N_c . These authors found⁸

$$N_c \rho (\langle R^2 \rangle_0 / M) = 2.3 \times 10^{-14} \text{ cm}^{-1} \quad (5)$$

where ρ is the density of the polymer.

Using the relation proposed by Vincent,²⁴ $S = m_0 / (N_a \rho l_0)$ (m_0 is the average molecular weight per main-chain bond, and N_a Avogadro's number), one obtains, by combining eqs. (1), (2), and (3),

$$N_c \rho (\langle R^2 \rangle_0 / M) = 185 / (N_a l_0) \quad (6)$$

Taking a typical value, $l_0 = 1.5 \times 10^{-8}$ cm, the value on the right side of eq. (6) is $2.1 \times 10^{-14} \text{ cm}^{-1}$, showing a good agreement with eq. (5).

On the other hand, the proposed correlation [eq. (3)] has the following main advantages compared with the literature correlations:

- (1) Most of the literature correlations provide a purely empirical relation between N_c (or M_c) with some structural parameters of the polymer chains. As they are not dimensionally consistent, the connection between the molecular nature of entanglements and the critical molecular weight is unclear. In contrast, the proposed correlation [eq. (3)] is very simple, and is dimensionally consistent. It is also clearly related to the well-known reptation ("tube") models.^{12,13} The reptation models state that polymer chains entangle when their end-to-end distance becomes larger than the "diameter" of the tube. Equation (3) suggests that molecules move freely in any direction if their end-to-end distance is shorter than $13.6D$, whereas entanglement behavior occurs when the end-to-end distance of polymer chains becomes larger than $13.6D$. Moreover, the proposed correlation indicates that the diameter of the tube, which has been taken as an adjustable variable in the reptation models,¹³ is a well-defined parameter, determined by the diameter of the polymer chains.
- (2) The literature correlations generally fit one kind of polymer (flexible, rigid, or semirigid) and fail for the others.⁹⁻¹¹ The proposed correlation holds true not only for flexible chains (this was found by other authors³⁻⁹), but also for semirigid chains such as for polymers with high characteristic ratio C_∞ (polysty-

rene and polyacrylamide) and for polymers containing para-aromatic rings (polycarbonate and polysulfone). This also suggests that the entanglements in polymers may arise from a common effect of interaction between end-to-end distance and diameter of polymer chains.

- (3) The proposed correlation has a relatively small standard deviation being equal to 0.11 for thirty six polymers. This is much better than the correlations available so far.

In summary, we propose a correlation relating the critical end-to-end distance for entanglements $\langle R_c \rangle$ to the polymer chain diameter D . This correlation is consistent with the reptation concept. Moreover, the proposed correlation holds true not only for flexible polymer chains, but also for semi-rigid chains. This suggests that the entanglements in polymers may arise for a common effect of topological interactions between the end-to-end distance and polymer chain diameter. This correlation also provides a simple method to predict the critical molecular weight M_c from polymer chain rigidity and cross-sectional area. For example, it predicts that poly(2-ethylbutyl methacrylate) would have a somewhat larger critical molecular weight than that found in the literature. Further experimental assessments of this correlation will be necessary to understand the universal entanglement behavior of polymers.

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ORGANIC COATINGS

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ZENO W. WICKS, JR. • FRANK N. JONES
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relationships by saying that adhesion requires that the liquid have a lower surface tension than the surface free energy of the substrate to be coated. From a practical standpoint, it is useful to do cruder but easier experiments. One can apply a drop of coating on a substrate, put the sample in an atmosphere saturated with the solvents in the coating, and watch the spreading. If the droplet of coating stays as a small ball, spreading is poor and adhesion problems should be expected. If the drop spreads out to a thin, wide circle, the coating meets at least one criterion for good adhesion. It is also useful to carry out a second type of experiment, in which a coating is spread mechanically on a substrate under a solvent saturated atmosphere and then observed. Generally, a liquid that spreads spontaneously in the first experiment will remain spread out in the second experiment. But sometimes, a liquid that spreads on the surface will draw up into droplets, or at least pull away in sections from the substrate when standing, without solvent evaporation.

Consider, for example, the application of *n*-octyl alcohol to a clean steel surface. The surface tension of *n*-octyl alcohol is lower than the surface free energy of steel, and it spreads on steel spontaneously. However, if one spreads out a film of *n*-octyl alcohol on steel, the film draws up to form droplets on the surface of the steel. The low surface tension of the *n*-octyl alcohol results from the linear hydrocarbon chain; however, after spreading on the polar surface of the steel, the hydroxyl groups of the *n*-octyl alcohol molecules interact with the surface so that a monolayer of oriented *n*-octyl alcohol molecules forms on the surface. This makes a new surface, aliphatic hydrocarbon, which has a low surface tension, lower than the surface tension of *n*-octyl alcohol. The *n*-octyl alcohol above a monolayer *dewets*. The behavior of *n*-octyl alcohol illustrates a principle important in formulating coatings: One must be careful about using additives with single polar groups and long hydrocarbon chains in coatings to be used directly on metals. An example is the poor adhesion to steel that can result from use of dodecylbenzenesulfonic acid as a catalyst (Section 11.3.1.1). Adhesion of latex films can be affected by a layer of surfactant forming at the interface between the coating and the substrate [10].

6.4. ADHESION TO METAL SURFACES

The metal and the surface characteristics of the metal can have major effects on adhesion; Ref. [11] provides a review of metal surface characteristics, cleaning, and treatments. The surface tension of a clean metal surface (usually, metal oxide) is higher than that of any potential coating. However, metal surfaces are frequently contaminated with oil, and such surfaces can have very low surface tensions. Whenever possible, it is desirable to clean the surface of the metal before applying a coating. Sometimes, the metal is wiped with rags wet with solvent. A more effective method is *vapor degreasing*, in which the object is hung from a conveyor that carries it into a tank above a boiling chlorinated solvent. The cold steel surface acts as a condenser, condensing solvent on the surface of the steel, where it dissolves oils. The solution drips off, removing the oil. The solvent is purified by distillation for reuse. Surfactant solutions are also used to clean oil from metals [11]. Care must be exercised in selecting surfactants and in rinsing the surface after cleaning. It is possible for some surfactants to adsorb on the surface, creating a hydrocarbon layer on the surface of the metal.

Steel can be cleaned by abrasive particle blasting such as sandblasting. (See Ref. [11] for a discussion.) The surface of the steel, including rust, is removed, leaving a rough surface. Sandblasting is widely used for steel structures such as bridges and tanks, but it leaves the

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Film Defects

Obvious defects can result from incomplete coverage during application of a coating, resulting in thin spots or holes, often called *skips* or *holidays*. Many other types of defects and imperfections can develop in a film during or after application. In this chapter we deal with the most important defects and to the extent possible, discuss the causes of the defects and approaches for eliminating or minimizing their occurrence. Unfortunately, the nomenclature for many defects is not uniform. Reference [1] provides definitions for coating terms, including those for film defects.

24.1. SURFACE TENSION

Many defects are related to *surface tension* phenomena. Surface tension occurs because the forces at an interface of a liquid differ from those within the liquid, due to the unsymmetrical force distributions on the surface molecules. The surface molecules possess higher free energy, equivalent to the energy per unit area required to remove the surface layer of molecules. The dimensions of surface tension are force exerted in the surface perpendicular to a line; SI units are newtons per meter or millinewtons per meter (mN m^{-1}). [Older units, still commonly used, are dynes per centimeter ($1 \text{ mN m}^{-1} = 1 \text{ dyne cm}^{-1}$).] Similar surface orientation effects are present in solids, which have surface free energies expressed in units of free energy per unit area, millijoules per square meter (mJ m^{-2}) that are numerically and dimensionally equal to mN m^{-1} . Frequently, people speak of the surface tension of the solids; although not formally correct, errors do not result, because the values are identical. Reference [2] is an excellent discussion of surface and interfacial properties, including data on many polymers.

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PHYSICAL CHEMISTRY
OF SURFACE PHENOMENA

Surface Tension of Tin and Its Alloys with Lead

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Abstract—The temperature and concentration dependencies of the surface tension of high-purity tin and its alloys with lead were investigated in an ultrahigh vacuum by the large-drop method. It was shown that the tin surface-tension polytherm obeyed the equation $\sigma(T) = 570.0 - 0.08(T - T_m)$. Lead was found to possess high surface activity in the range of its low concentrations in tin. Estimate was made for the limiting lead surface activity in tin-based alloys. Our conclusions about lead surface activity in alloys with tin are consistent with the literature data obtained by the modern electron-spectrometric methods for the surface compositions of the alloys studied.

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Tin, lead, and their alloys have found wide use in technology as solders, various additives, etc. For this reason, the surface properties of these metals and their alloys have become the object of a number of investigations [1–8]. However, the data presented in these works are consistent with each other neither quantitatively nor qualitatively. The main results of the recent studies on the temperature dependence of the surface tension (ST)

$$\sigma(T) = a - b(T - T_m) \quad (1)$$

are summarized in Table 1. It follows from this table and handbook [2] that the literature data on the tin ST at melting temperature lie in a wide range from 510 to 645 mN/m; i.e., the spread $\Delta\sigma_m \approx 135$ mN/m of the corresponding values exceeds measurement errors of 3% by a factor of 7 and errors of 1% by a factor of 20. Moreover, depending on the method used (gas-bubble maximum-pressure method, large-drop method, or contactless method), the difference between the measured ST values for tin can be as large as $\Delta\sigma \approx 80$ mN/m, suggesting that there may be possible failings in the methods of ST determination, the violation of thermodynamic equilibrium in measurements, etc. [9, 10]. In our opinion, this primarily applies to the contactless methods of ST determination. For instance, the values obtained in [10] for the tin ST (at T_m) by two different methods were 551 and 630 mN/m.

There is also a qualitative discrepancy between the literature data on the concentration dependence of ST in a binary tin-lead system. This is evident from the fact that some of the authors observe maxima and minima in the surface tension $\sigma(x)$ and density isotherms of the Pb–Sn system [4–6], whereas, according to the other authors, the $\sigma(x)$ isotherms for this system are smooth curves without any singularities over the whole range of concentrations [2, 20]. For instance, according to [6], the concentration dependence of the ST $\sigma(x)$ for the

Sn–Pb system shows a maximum corresponding to the eutectic composition (Pb + 62% Sn), whereas, from the results in [4], it follows that this alloy composition corresponds to a minimum in the $\sigma(x)$ isotherm.

The ST temperature coefficients obtained by different authors also differ severalfold, suggesting that many of the available literature data on $d\sigma/dT$ are not sufficiently reliable and that these data require certain improvement [18, 21].

In this work, we studied the quantity $\sigma(T)$ for pure tin and the temperature and concentration dependencies of ST for tin-based lead alloys.

EXPERIMENTAL

In studying the temperature and concentration dependencies of the surface tension of metal melts, we chose the large-drop method with the use of an all-soldered measuring cell. This method has the advantage of providing strict identity of sample-preparation and measurement conditions [22]. Starting components with a content of no less than 99.99% main element were used for sample preparation. The main impurities in Sn (OVCh-000) were: Pb ($1 \times 10^{-5}\%$), Zn ($<3 \times 10^{-5}\%$), Bi ($<2 \times 10^{-6}\%$), Ga ($1 \times 10^{-5}\%$), and In ($<5 \times 10^{-6}\%$). We used SO brand lead (GOST 3778-77), for which the total content of metal impurities did not exceed 8×10^{-3} wt %.

Alloys of different compositions were prepared from tin and lead by gradually diluting tin with portions of liquid lead, as described in [23, 24]. A liquid-metal droplet was placed on a substrate shaped like a cup with strictly circular, “threaded by knife,” upper cut so that the droplet on the surface had a strictly axisymmetric shape and maximum diameter.

The starting pure metals were additionally subjected to thermovacuum treatment for 5, 6 h at 1000 K on an

Table 1. Temperature dependence [Eq. (1)] of the surface tension (mN/m) of liquid tin

Method	a	b	ΔT , K	Notes
LDM [11]	613	0.17	T_m-873	Surface purification by ion (Ar^+) etching. Auger spectroscopy monitoring
GBMPM [12]	573 ± 2	0.069	505–873	Measurements on tin samples with a content of no less than 99.99%. Argon as a working gas. Corundum capillaries. Temperature control with an accuracy of ± 3 K
SDM [10]	551	0.09	510–1820	Small Sn droplet in an $Ar + H_2$ medium; tin with a content of no less than 99.99%; alumina or graphite substrate
CM [10]	630	0.13	1380–1750	Atmosphere of mixed purified argon and hydrogen
LDM [13]	$\sigma(T) = 598$		560	99.9999-purity 1 g tin samples. Ion etching of liquid samples (ion current $I = 30$ mA at $E = 3$ keV)
LDM [14]	$\sigma(T) = 507$		970	In helium at a pressure of 5×10^4 Pa. Tin samples with a content of 99.999% main element
DMPM [15]	543.4	0.080	523–723	Vacuum measurements at 5×10^{-5} Pa on OVCh-000 tin samples
LDM [16]	645	0.10	T_m-773	Vacuum measurements. Tin samples with a content of 99.999 at % main element
LDM [17]	645	0.160	T_m-773	Ultrahigh-vacuum measurements. Tin samples with a content of 99.999 at % main element. Surface purification by ion (argon) bombardment
[2]	544.0	0.076	T_m-1683	Recommended value for $\sigma(T)$ from the analysis of the experimental data published until 1976
[18]	561.6	0.103		Recommended value for $\sigma(T)$ averaged over the experimental data on $\sigma(T)$ and $d\sigma/dT$ published until 1992
[18]	585.7	0.124		Recommended value for $\sigma(T)$ averaged over 12 works, in which the tin $\sigma(T)$ values are the highest (among the experimental values published until 1992)
[19]	580.0	0.09		Recommended values for $\sigma(T)$
LDM*	570.0	0.08	T_m-623	Vacuum measurements at 1×10^{-7} Pa. Tin of the OVCh-000 grade

Note: LDM = large-drop method; SDM = sessile-drop method; DMPM = droplet maximum-pressure method; GBMPM = gas-bubble maximum-pressure method; CM = contactless methods. Asterisked are the data of this work.

ultrahigh-vacuum pumping station ($\sim 10^{-7}$ Pa) to purify them of potential oxides that could arise when loading metals into the measuring cell. To do this, pieces of each of the metal components were put into separate (for each component) quartz glasses inserted into one another. Their open bottom ends were drawn off to form thin (0.4 mm) capillaries. The pieces were preliminarily weighed and placed into two (for Sn and Pb, respectively) vertically mounted quartz bins equipped with autonomous heaters. The bins were soldered onto the top of the all-soldered measuring cell via a “quartz-molybdenum glass” transition layer. During thermal treatment, the liquid metal components were held in the uppermost glasses by special quartz rods. This gave rise to gas separation and concentration of the potential oxides at the surfaces of the liquid metal components.

5, 6 h after high-temperature treatment, the gate rods were sequentially raised up a little by electromagnets, and the melts were slowly pressed through the thin capillaries; they left their surface portions in each of the upper glasses. After liquid metals entered the measuring cell, both filling bins with glasses were unsoldered from the main device (measuring cell), and each of the

glasses with capillaries containing metal residues was withdrawn from the bin and weighed separately on an analytical balance to determine the true mass of each component entering the device.

The measuring cell with the filtered metals was left on the pumping station and additionally subjected to joint thermovacuum treatment at 750 K for several more hours, whereupon it was unsoldered from the pumping station and immediately mounted on a rotating air thermostat preliminarily heated to 700 K. In measuring the ST, a gradientless thermal field was produced inside the thermostat and controlled with an accuracy of ± 0.2 K by chromel-alumel thermocouple transducers.

The droplet samples were photographed by a camera with a long-distance ($F = 0.3$ m) objective of the I-37 type, allowing high-quality negative images to be obtained with a $\times 5$ magnification. The droplet photographs were measured on a UIM-21 microscope and processed by the standard method [22, 25].

The error in the compositions of the prepared alloys was 0.1 wt %. Since the ST was determined using formula involving alloy density, the total measurement error in surface tension, with allowance for the error in

measuring the density of Sn melts and Sn alloys with Pb, was ~1.5%.

RESULTS AND DISCUSSION

The least-squares results on the temperature and concentration dependencies of the STs of tin and its alloys with lead are presented graphically in Fig. 1 and, in the form of approximating equations, in Table 2. One can see in Fig. 1 that, in the temperature range studied, the ST polytherms of pure tin and its alloys with lead are straight lines. In particular, the temperature dependence of the ST for pure tin obeys Eq. (1), where σ is in mN/m, T in K, $a = 570.0$, and $b = 0.08$.

Our data on the ST of pure tin (at T_m) agree well with the results obtained in [12] by the gas-bubble (purified argon) maximum-pressure method with corundum capillaries. A comparison with the literature ST values for tin at melting temperature shows that our data are 10 mN/m lower than the value recommended by Popel' in [19] and exceeds by 26 mN/m the handbook value [1]. Curiously, a value of 545 mN/m reported earlier by Popel' for the tin ST [26] is 35 mN/m lower than the value given for this element in his monograph [19]. This fact correlates with the general trend that is also pointed out by the other authors: with the progress of vacuum technology and improvement of experimental vacuum conditions, as well as of the technology of purifying and monitoring the surface states of samples by the electron-spectrometric methods, the ST values of pure metals slightly "rise" [19, 27]. On the other hand, the values of 613 and 645 mN/m given, respectively, in [11] and [17] for the tin ST (at the melting point) are, in our opinion, unjustifiedly overstated for the reasons listed in [23].

Particular attention should be given to one of the latest fundamental reviews [18], where the literature results published until 1992 on $\sigma(T)$ of pure liquid metals were also presented. Although the analysis performed by the author of [18] of the experimental data for ST is, in our opinion, not quite comprehensive (in [18], the results given for $\sigma(T)$ in some groups of works, in which, e.g., the ST values obtained for tin were the highest, were merely summed up and averaged), it seems, nevertheless, worthwhile to compare our data on the tin $\sigma(T)$ with those recommended in [18] (Table 1).

It follows from Table 1 that our data on the tin ST (at T_m) exceed by 8.4 mN/m the corresponding "totally-averaged" data and are lower by 24 mN/m than the data "averaged over 12 works," in which the values of tin ST were the highest among all the experimental data published in the literature until 1992.

We used the temperature dependencies for the STs of the Sn-Pb alloys (Table 2) to construct the isothermal section of $\sigma(x)$ for a temperature of 573 K (shown graphically in Fig. 2). One can see in Fig. 2 that even small additions of lead to tin noticeably decrease the ST of alloys; at 573 K, the tin surface tension decreases by

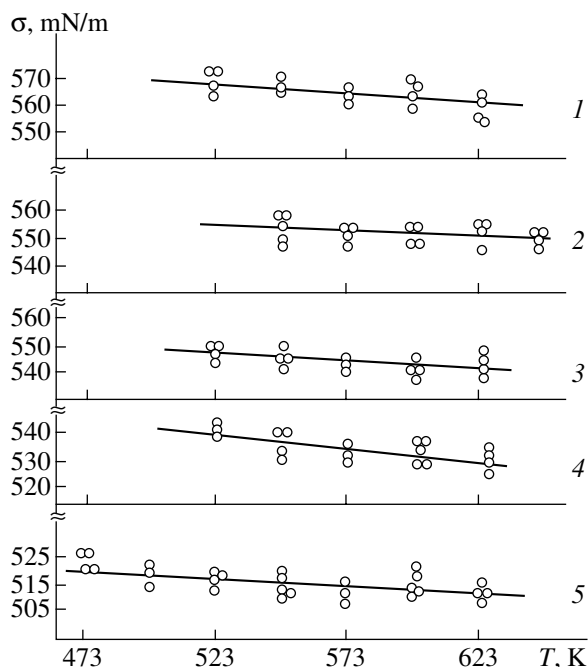


Fig. 1. Temperature and concentration dependences of the ST for tin and its alloys. 1, Pure tin; 2, Sn + 1.05 at % Pb; 3, Sn + 2.54 at % Pb; 4, Sn + 6.49 at % Pb; 5, Sn + 25.93 at % Pb.

30 mN/m upon the addition of 5 at % Pb. Our estimates suggest that the limiting lead surface activity (G) in the alloys with tin is

$$G = \lim_{x_{\text{Pb}} \rightarrow 0} (\Delta\sigma/\Delta x) \approx 1200 \text{ mN}/(\text{m at. fraction}).$$

Note that the error in G was ~15%, because we used the graphical method for the differentiation of the ST isotherm $\sigma(x)$ for the tin-lead system.

A rather high surface activity obtained in this work for lead in its tin-based alloys correlates with the main criteria for the surface activity of the components in a

Table 2. Temperature and concentration dependences of the surface tension of pure tin and Sn-Pb alloys

[Pb], at %	a	b	T_m	ΔT , K
0	570.0	0.08	505	505–623
1.05	554.3	0.05	503.5	503.5–643
2.54	548.0	0.06	501.5	501.5–623
4.28	543.3	0.08	497.1	497.1–623
6.49	543.2	0.12	493.0	493.0–623
9.20	536.9	0.08	485.8	485.8–623
12.34	532.7	0.07	478.9	478.9–623
17.69	527.8	0.08	468.8	468.8–623
21.49	525.8	0.11	462.5	462.5–623
25.93	520.1	0.08	457.2	457.2–623
31.42	512.4	0.08	473.9	473.9–623

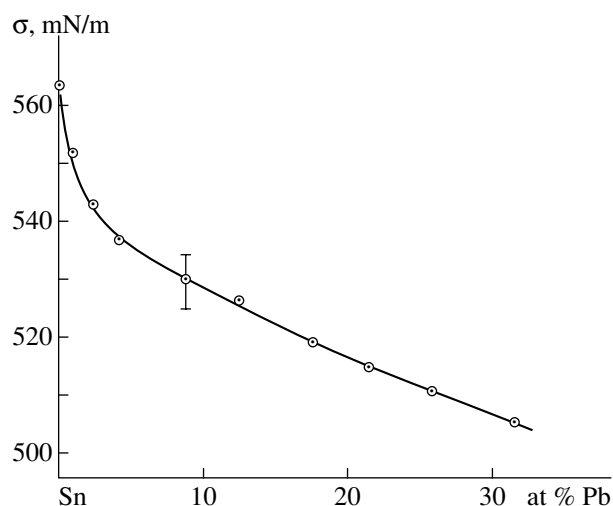


Fig. 2. ST isotherm for the Sn–Pb alloys at 573 K.

binary metal alloy, e.g., for their atomic volumes, surface-tension ratio of the pure components, potential barrier at the metal surface, etc. [19]. Such a high activity is also confirmed by the results of studying the composition of surface layers in tin-lead alloys by the modern electron-spectrometric methods [17, 28]. In particular, it follows from the data given in [17, 28] that lead dominates at alloy surfaces in binary tin-lead solutions throughout the whole concentration range of compositions. Moreover, according to the data in [17], no noticeable changes in the surface compositions of the solutions studied occur with a rise in temperature. In our opinion, this explains the linear dependence for the $\sigma(T)$ polytherms obtained in our work (Fig. 1). Thus, the data obtained in this work on the decisive role of lead as a surface-active component in the tin-lead system are consistent with the known data on the surface compositions of Sn–Pb alloys.

CONCLUSIONS

In conclusion, the temperature and concentration dependences of the surface tension of pure tin and tin-based lead alloys have been studied in this work. The data obtained on the surface activity of the tin-based lead alloys are consistent with the main criteria for the surface activity of the components and are in agreement with the literature data obtained by the modern electron-spectroscopic methods for the surface compositions of the alloys under study.

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Fundamentals of Adhesion

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ADHESION THEORIES AND MECHANISMS

Adhesion occurs when two bodies are held together by intimate interfacial molecular contact in such a way that a unit is formed. Adhesion is a complex phenomenon related to physical effects and chemical reactions in the "interface." Multiplicity of interfaces in a typical industrial coating system is shown in Figure 1. Since each identifiable surface usually will have several layers of adsorbed or chemisorbed molecules associated with it, the number of actual interfaces is unknown. The question is where to draw the line between two surfaces and where actually the adhesion takes place.

Adhesive forces are set up as the coating is applied to the substrate and during curing or drying. The magnitude of these forces will depend on the nature of the surface and the binder (resin, polymer, vehicle). These forces may be broadly categorized as one of two types, primary valency forces and secondary valency forces (Table 1). Chemical bonds are examples of the primary valency forces and provide much higher adhesion values than do the secondary forces. Secondary valency bonding is based on much weaker physical forces typified by hydrogen bonds. These forces are more likely to be found in materials having polar groups such as carboxylic acid functionalities than on nonpolar surfaces such as polyethylene.

The actual mechanism of coating attachment is not yet fully understood. However, the forces holding the two bodies together (the paint and the substrate) may be of mechanical interlocking, by way of paint diffusion, electrostatic attraction or true chemical bonding between coating and the substrate. Depending on the chemistry and physics of both substrate surface and the coating used, one or a combination of these postulated mechanisms may be involved. Some of the theories suggested are discussed below.

1. MECHANICAL THEORY: This mechanism of coating action occurs when the substrate surface upon which the coating is spread contains pores, holes, crevices, and voids into which the coating solidifies. In this manner the coating, much like a nail in a wood assembly, acts as a mechanical anchor. If the substrate has undercut areas that are filled with cured coating, a mechanical component makes removal of the coating even more difficult, analogous to holding two dovetailed pieces of wood together. Many instrumental analyses and mapping (profile) of various surfaces indicate that the coating can indeed penetrate to complex tunnel shaped undercuts and cracks where, upon curing to a hard mass, it provides mechanical attachment. Adhesion of coatings and various paints to old and weathered coatings as well as adhesion to sand blasted substrates are examples of this type of adhesion mechanism. Iron or zinc phosphate tend to provide larger

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contact area for coatings and thus enhance adhesion and corrosion resistance. Figure 2 illustrates a hypothetical profile of a substrate surface and a coating penetration.

Surface roughness affects the interfacial area between the coating and the substrate. Because the forces required to remove coatings are related to the geometric surface area, whereas the forces holding the coating on to the substrate are related to the actual interfacial contact area, the difficulty of removing a coating can be increased by increasing the surface area. This usually can be accomplished by surface roughening by various mechanical abrasion methods. Comparison of surface cross section of geometric area and the actual interfacial area is given in Figure 3. The actual interfacial contact area is generally several times larger than the geometric area. The increase in adhesion as a result of an increase in surface area by sanding is illustrated in Figure 4. Obviously due to many other factors, the adhesion will not increase in the same proportion, but noticeable increases are usually observed.

Greater surface roughness is only advantageous if the coating penetrates completely into all irregularities of the surface. Failure to completely penetrate can lead to less coating to interface contact than the corresponding geometric area and will leave voids between the coating and the substrate. Trapped air bubbles in voids allow accumulation of moisture and eventually loss of adhesion will result.

Quite often intercoat adhesion (particularly in automotive coatings) can be improved by scuff sanding the previous cured coating. Especially in the case of basecoat/clearcoat systems where the clearcoat is designed to be smooth, glossy, and with low surface tension, adhesion of the second coat takes place with some difficulties. The problem is even more severe when such a cured coating is baked at considerably higher temperatures than the intended original bake and/or its cure time is extended. In both of these cases, light sanding of the immediate surface has been shown to dramatically improve the adhesion. Although surface roughening generally improves the adhesion, care must be taken to avoid deep and sharp profiles. Deep hills generated by roughening may cause telegraphing (read through) which in some cases may not be desirable. In addition, sharp and deep hills allow the formation of non-uniform films which act as stress points that tend to reduce the coating durability by weakening the adhesion. As long as the films are somewhat fluid, the shrinkage, uneven depths, and three-dimensional changes introduce little unrelieved stress. As viscosity and film stiffness increase and as film adhesion to the substrate develops, substantial stresses are accumulated

Table 1—Bonding Forces and Binding Energies

Force	Type	Energy	Example kcal/mole
Covalent	Primary	15-170	Most organics
Hydrogen bond ...	Secondary	<12	Water
Dispersion	Secondary	<10	Most molecules
Dipole	Secondary	<5	Polar organics
Induction	Secondary	<0.5	Non-polar organics

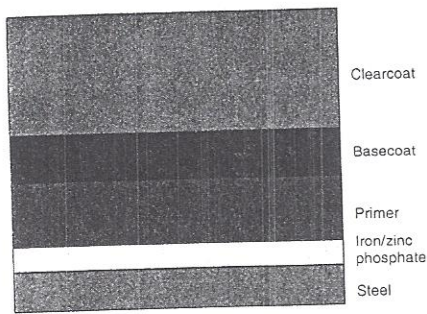


Figure 1—Schematic representation of cross-section of a typical automotive coating system

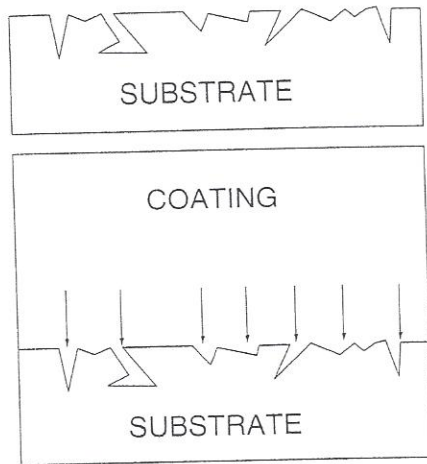


Figure 2—Schematic representation of hypothetical surface profile and a mechanical adhesion

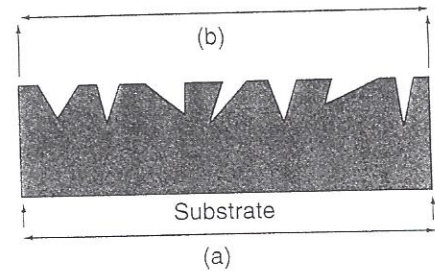


Figure 3—Surface cross-section comparison of (a) geometric area and (b) actual interfacial coating area

and retained in the dry film. Obviously under the fixed application parameters (wet and dry film thickness) the film thickness on top of hills will be less than the valleys, affording variable physical properties. The resultant non-uniform film with high levels of internal stress will enter the service environment where it will be further subjected to solvent attack from repair coatings or weathering, occasionally pushing such films beyond their capacity for stress. Cracking or delamination or other evidence of lost film integrity will be the result.

The adhesion of metal platings to polypropylene and ABS plastics has been shown to arise from mechanical interlocking.^{1,2} The metal plating process involves first treating the plastic surface to produce numerous cavities capable of mechanical interlocking, sensitizing with stannous chloride solution, activating by depositing Pd⁰ from Pd²⁺ solution, depositing electroless nickel and then electroplating the desired metal, such as chromium.¹ Strong adhesion of the metal plating to the plastics is obtained only when the plastics have been pre-treated to produce interlocking cavities.^{1,3} Various metal pre-treatments⁴ may not only change the surface chemical compositions, but also produce interlocking surface sites. Mechanical interlocking contributes greatly, if not critically, to adhesion to such surfaces. Figure 5 shows the surface topography of an original and phosphate treated cold-rolled steel. The original surface is relatively featureless and smooth. After phosphating, numerous intermeshing platelets of iron phosphate crystals can be seen on the surface. The interplatelet spaces provide numerous interlocking sites.

2. CHEMICAL BONDING THEORY: The formation of covalent chemical bonds across the interface is possible and very likely takes place in thermoset coatings. This type of bonding is expected to be the strongest and most durable. It does however, require that there be mutually reactive chemical groups tightly bound on the substrate surface and in the coating. Chemical bonding at the interface is difficult to detect, mostly because of the thinness of the interface. However, as will be discussed, interfacial bonding has been shown to occur, and greatly contributes to the adhesion strength. Some surfaces, such as previously coated surfaces, wood, composites and some plastics, contain various chemical functional groups which, under appropriate condition, can produce chemical bonds with the coating material. Some functional groups capable of forming chemical interactions are shown in Figure 6.

Organosilanes are widely used as primers on glass fibers to promote the adhesion between the resin and the glass in fiberglass-reinforced plastics.^{5,6} They are also used as primers or integral blends to promote adhesion of resins to minerals,

metals, and plastics. Essentially, during application, silanol groups are produced which then react with the silanol groups on the glass surface or possibly with other metal oxide groups to form strong ether linkages. Figure 7 illustrates this type of chemical bonding which may take place between a silane functional coating and metal hydroxide on the surface of glass, ceramics, and some metallic substrates.

Coatings containing reactive functional groups such as hydroxyl or carboxyl moieties tend to adhere more tenaciously to substrates containing similar groups. One example of the existence of such a mechanism is the superior adhesion of melamine cured acrylic topcoats over melamine cured polyester primers. One possible explanation is that the residual unreacted hydroxyl functional groups on the surface of the (cured) primer react with melamine curing agents in the topcoat, essentially tying the topcoat to the primer layer. When such a primer is overbaked (longer times and/or higher bake situations), adhesion of topcoat becomes noticeably weak and occasionally nonexistent. The evidence for a possible contribution from the residual hydroxyl come from the fact that the IR spectra of the standard baked primer is rich in hydroxyl groups, (spectrum a) while the overbaked primer (spectrum b) contains very little, if any, hydroxyl functional groups (Figure 8). The schematic presentation of the surface chemistry of a standard and overbaked primer and the effect on topcoat adhesion is shown in Figure 9.

Chemical bonding also may occur when a substrate contains reactive hydroxyl groups which under an appropriate condition, may react with isocyanate groups from the incoming coating in thermoset polyurethane coatings

Most likely chemical bonding accounts for the strong adhesion between an epoxy coating and a substrate with a cellulose interface. Obviously epoxy groups of an epoxy resin react with the hydroxyl groups of a cellulose at the interface, as evidenced by IR spectroscopy. The chemi-

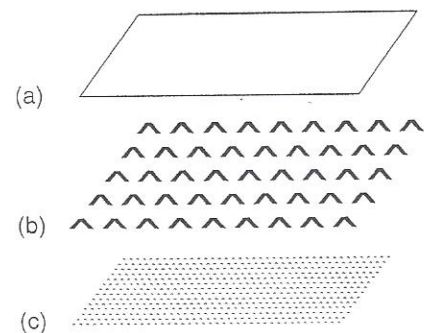


Figure 4—Surface roughness and increase in actual contact area by means of sanding

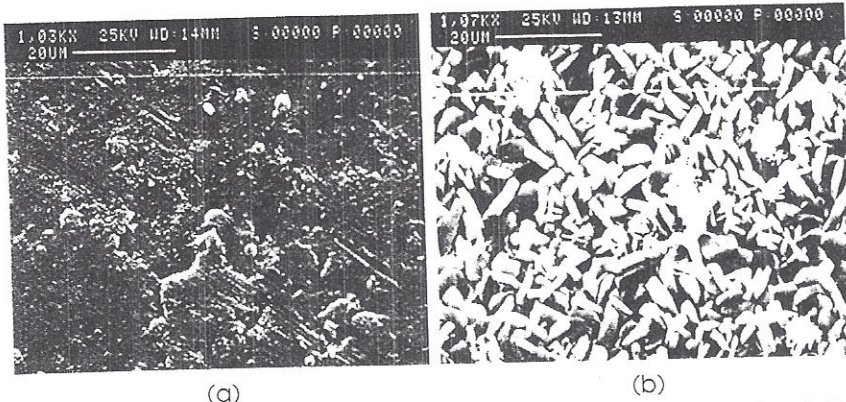
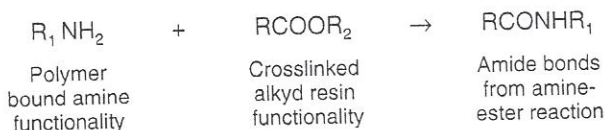


Figure 5—Surface topography of an (a) untreated and (b) phosphate treated cold rolled steel. (Henkel Corp., Parker Amchem, Madison Heights, MI)

cal reaction causes the OH stretching band at 3350 cm^{-1} and the C—O stretching bands at $1100\text{--}1500\text{ cm}^{-1}$ of the cellulose to diminish, and the epoxide band at 915 cm^{-1} and the anti-symmetric O-bridge stretching band at 1160 cm^{-1} of epoxy resin to disappear.⁷ A representative reaction of cellulose molecule with an epoxy functionality is shown in Figure 10.

Some polymers adhere weakly to crosslinked polymeric surfaces, failing interfacially. Incorporation of a small amount of certain nitrogen-containing groups has been claimed to greatly enhance the adhesion.^{8,9} An example is the strong adhesion of an amino polymer to a crosslinked alkyd resin, due to interfacial amine-ester interchange reaction between the two phases to form amide bonds.



The amine-ester interchange reaction can readily be seen by using butylamine as a model compound for the amino polymer. When this amine is added to a toluene solution of an uncured alkyd resin, it readily reacts with the latter at room temperature to form dibutyl phthalamide, which crystallizes and precipitates out.

A mixture of an amino polymer and an uncured alkyd resin was examined by FTIR spectroscopy. After baking the mixture, the amino absorption band decreases with concurrent appearance of the amide absorption band, suggesting that amin-ester interchange reaction can indeed occur at the interface.

3. ELECTROSTATIC THEORY: It is conceivable that electrostatic forces in the form of an electrical double layer are formed at the coating-surface interface. Both coatings and surfaces contain residual electrical charges dispersed throughout the system. Interaction between these charges could account for some adhesion. Electrostatic forces are primarily dispersion forces, and forces arising from the interaction of permanent dipoles. One important attractive force between molecules of a substance that possesses a permanent dipole moment is the *dipole-dipole attraction* between the positively polarized region of one molecule and the negatively polarized region of the other. Induced dipole-induced dipole attractions, called *London forces*, or dispersion forces which are one type of *van der Waals force*, also contribute to adhesion. For certain substrate/coating systems, these forces provide much of the attraction between the coating and surface. It should be noted that such interactions are only operational on a very short range and their effectiveness decreases with the sixth or seventh power of the distance of separation. Because

neither of these forces is significant beyond about 0.5 nm (5 \AA), the need for intimate contact between coating and surface becomes obvious.

4. DIFFUSION THEORY: When two phases of coating and the substrate (polymeric) attain molecular contact by wetting, segments of the macromolecules will diffuse across the interface to various extents, depending on material properties and curing conditions. The phenomenon is a two-stage process; wetting is followed by interdiffusion of chain segments across the interface to establish the entangled network as shown in Figure 11.

Dissimilar polymers are usually incompatible because of their long chain nature and their low diffusion coefficients. Consequently, diffusion of an entire macromolecule across the interface is unlikely. However, both theory and experimental data show that local segmental interdiffusion can occur readily forming a diffuse interfacial layer $10\text{--}1000\text{ \AA}$ between two polymers. Indirect evidence of diffusion of coatings includes the effect of contact time, cure temperature, pressure, and molecular structure (molecular weight, chain flexibility, side group, polarity, double bond, and physical compatibility). Direct evidence includes the measurement of diffusion coefficient^{10,11} and observation of interfacial structure by electron microscopy,¹² radiothermoluminescence techniques, and optical microscopy. Obviously, this type of diffusion can best take place in polymeric substrates such as engineering plastics, where the free volume between molecules is large and molecules are much farther apart from each other as compared with metallic substrates.

MECHANICS OF ADHESION DEVELOPMENT

When two dissimilar materials are brought into "intimate" contact, a new interface is formed at the expense of two free surfaces in air. The nature of the interaction of the interface determines the strength of the bond which forms between the coating and the substrate. The extent of these interactions is greatly determined by the wettability of one phase by the other. In the case of coatings that are applied in liquid state, mobility of the coating phase is also of great help. Wetting, therefore, may be viewed as intimate contact between a coating and a substrate. Schematic representation of compete and

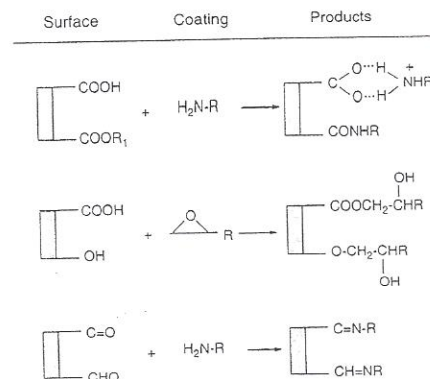


Figure 6—Possible relationships of surface functionalities with amine and epoxy-containing coatings

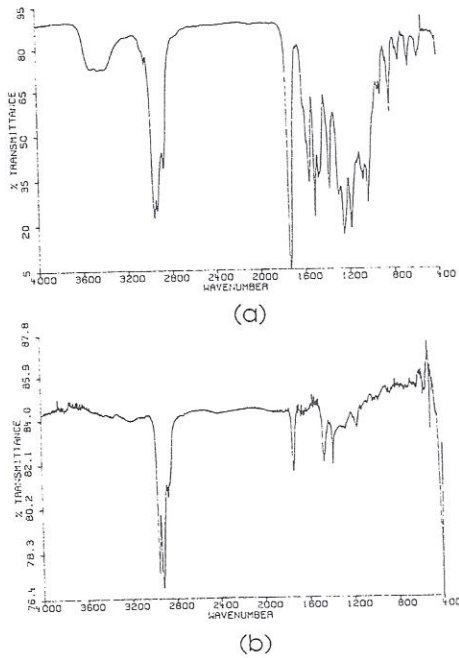
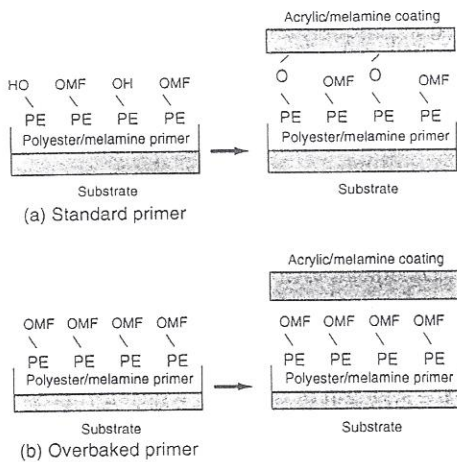


Figure 8—Comparison infrared spectra of (a) standard baked (cured) and (b) overbaked primer coat



PE = Polyester; MF = Melamine-Formaldehyde

Figure 9—Schematic representation of surface chemistry of (a) a standard and (b) overbaked primer and its effect on the adhesion to topcoat

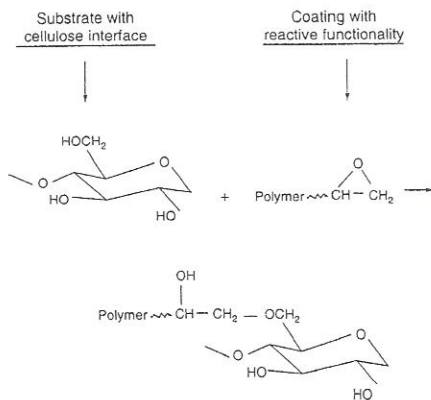


Figure 10—Partial chemical structure of cellulose molecule and its representative reaction with epoxy functionality

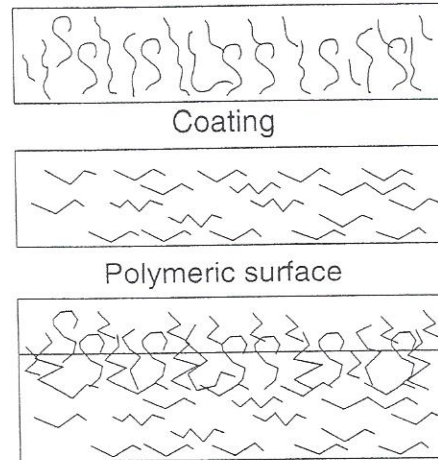


Figure 11—Schematics of diffusion of coatings in polymeric medium

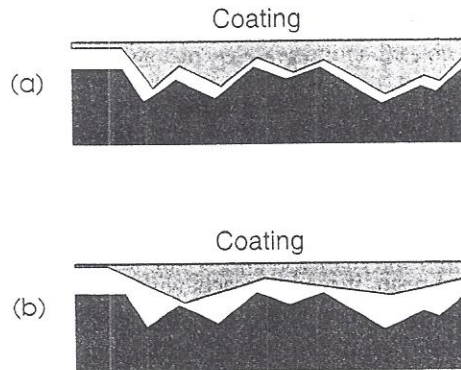


Figure 12—Schematic representation of (a) good wetting and (b) incomplete wetting

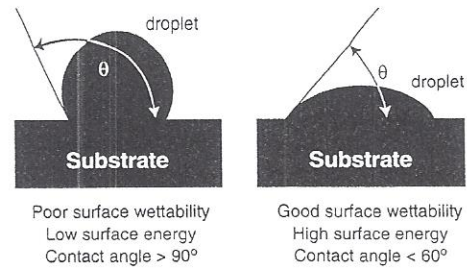


Figure 13—The degree to which a liquid coating wets a solid surface is measured by the contact angle θ

incomplete wetting is shown in Figure 12. In addition to initial wetting, in order for adhesion to remain between substrate and the coating it is important that intimate wetting and bonds remain intact after the coating has solidified.

Coatings solidify as a result of:

- (a) cooling to below the melting temperature (glass transition temperature, T_g), or
- (b) a chemical crosslinking reaction, or
- (c) evaporation of solvents and diluents.

An example of a type (a) coating is the thermoplastic powder coating or the melt extrusion lamination of polymers to metals and to other polymers. Type (b) coatings include one- and two-part crosslinkable epoxy, polyurethane, or melamine cured acrylic systems. Printing inks and lacquer paints are examples of type (c) coatings where the pigment binders may also have some crosslinking ability on drying. The wetting of substrates by coatings is, therefore, central to bond formation and, hence, to adhesion.

1. WETTABILITY AND SURFACE ENERGETICS: Wetting is a necessary criteria for adhesion. Mechanisms of adhesion previously discussed are only operational if, and only if, effective wetting is present between the coating and the substrates. The wetting of a surface can be described in thermodynamic terms. The surface tension of the coating in its liquid state and the surface energetics of both the substrate and the solid coating are important parameters which can influence the strength of the interfacial bond and adhesion development.

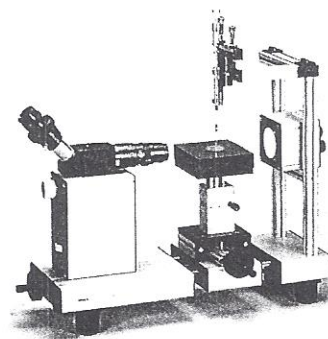
The molecules or atoms at the surface of a homogeneous solid or liquid are in a different environment from those in the interior. In the interior, each molecule is surrounded by similar ones, and the average distance between them is governed by the trade-off between attractive forces pulling the molecules together and strong repulsive forces that prevent different molecules from occupying the same space. Molecules at the surface, however, are no longer attracted equally in all directions. They interact somewhat with the substance, normally air, lying above the surface, while they are attracted inwards by the molecules lying below the surface. The attraction of the underlying molecules tends to pull them inwards, minimizing the number of molecules at the surface, and hence, the surface area. This attraction gives rise to the *surface tension* of liquids and accounts for a liquid droplet behaving as though it were covered by an elastic skin. In addition, the surface molecules are generally at a greater intermolecular spacing than in the bulk and are therefore in a state of higher energy. Work must be supplied to move molecules from the interior to the surface. The increase in the Helmholtz free energy accompanying a unit increase in the surface area of a liquid is, by definition, the surface tension.

2. INTERFACIAL THERMODYNAMICS: The degree to which a liquid coating wets a solid surface is measured by the contact angle (θ) as illustrated in Figure 13. When $\theta = 0$, the liquid spreads freely over the surface and is said to completely wet it. Complete wetting occurs when the molecular attraction between the liquid and solid molecules is greater than that between similar liquid molecules.¹³ The surface tensions are related to the contact angle by an expression from equilibrium consideration.¹⁴

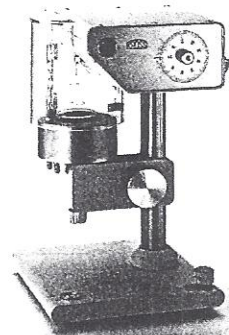
$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$$

Where γ_{sv} is solid/vapor surface tension; γ_{sl} is solid/liquid surface tension; and γ_{lv} is liquid/vapor surface tension. The surface tension γ_{sv} of a solid that has absorbed a layer of vapor is generally less than that of the solid *in vacuo* γ_s and this reduction is termed the spreading pressure π_s .

$$\pi_s = \gamma_s - \gamma_{sv}$$



(a)



(b)

Figure 14—Typical contact angle meter and (b) interfacial tensiometer. (Krusz USA, Charlotte, NC)

However, the liquid surface tension is little affected by the vapor phase, so that $\gamma_{lv} = \gamma_l$. Whether or not a given coating will wet a solid surface depends on the surface tension of both substances. The ability of a liquid to wet and spread on a solid is often described by the spreading coefficient S_{sl} , which is related to the surface tension:

$$S_{sl} = \gamma_{sv} - \gamma_{sl} - \gamma_{lv}$$

A large positive S_{sl} implies that a liquid will spontaneously wet and spread on the solid. A negative S_{sl} implies lack of wetting and spreading by the liquid and the existence of a finite contact angle, $\theta > 0$.

3. CONTACT ANGLE AND CRITICAL SURFACE TENSION: A widely-used method for determining the surface tension of a solid has been developed using contact angle measurements. The calcu-

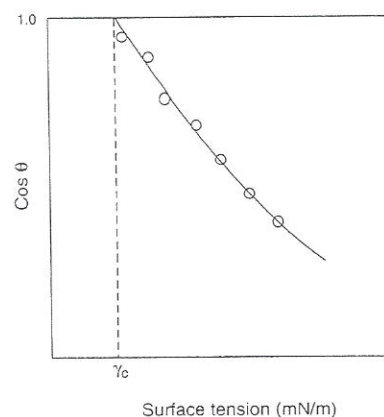


Figure 15—Critical surface tension by Zisman plot for a particular solid surface and a homologous series of liquids

Table 2—Surface Tensions of Typical Solvents Used in Coatings

Solvent	Surface Tension dynes/cm
Water	72.7
Ethylene glycol	48.4
Propylene glycol	36.0
o-Xylene	30.0
Toluene	28.4
n-Butyl acetate	25.2
n-Butanol	24.6
Mineral spirits	24.0
Methyl isobutyl ketone	23.6
Methanol	23.6
VM&P naphtha	22.0
n-Octane	21.8
Lactol spirits	19.9
n-Hexane	18.4

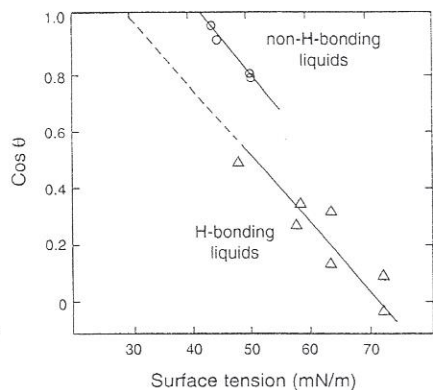


Figure 16—Comparison of Zisman plots of H-bonding and non-H-bonding liquids on polystyrene. (Data taken from reference 25)

Table 3—Surface Tensions of Typical Polymers and Additives Used in Coatings

Polymer	Surface Tension dynes/cm
Melamine resin	57.6
Polyvinyl butyral	53.6
Benzoguanamine resin	52
Poly(hexamethylene adipamide)	46.5
Epon 828®	46
Urea resin	45
Polyester melamine film	44.9
Polyethylene oxide diol Mw 6,000	42.9
Polystyrene	42.6
Polyvinyl chloride	41.9
Polymethyl methacrylate	41
65% Soya FA alkyd	38
Polyvinyl acetate	36.5
Polybutyl methacrylate	34.6
Poly(n-butyl acrylate) Mn 32,000	33.7
Modaflow®	32
Polytetrafluoroethylene Mw 1,088	21.5
Polydimethyl siloxane Mn 1,200	19.8
Polydimethyl siloxane Mn 162	15.7

lation of surface free energy from contact angle measurements has been the subject of much controversy. This subject still remains unresolved because the surface free energy of a solid cannot be measured directly. However, it is not the intention of this monograph to debate all the different issues, but to provide a sound guide for the practitioner through the array of conflicting ideas so that the reader can make a first step in estimating thermodynamic parameters of surfaces.

Approximate and apparent contact angle can be measured by contact angle meters available from various test equipment suppliers. One such device is depicted in Figure 14. In this method a drop of several different kinds of liquids is put on the desired surface and the angle is measured. One measure of the quality of a surface is the critical surface tension, γ_c . This surface energy is determined by measuring the contact angle of a series of liquids on the surface, plotting the cosines of the angles versus the surface tension of the respective liquids, and extrapolating to $\cos \theta = 1$ ($\theta = 0^\circ$), as in Figure 15. The extrapolated surface tension is called the critical surface tension of the surface. For example, following the above procedure, the critical surface tension polyethylene is determined to be 31 dynes/cm. All liquids with surface tensions equal to, or less than, the critical surface tension will spontaneously spread on the surface if applied as a drop. Therefore, an epoxy resin which exhibits a surface tension of 47 dynes/cm will not wet the polyethylene surface. On the other hand, a silicone mold release agent with a surface tension of 24 dynes/cm will spread on the surface.

The development of this concept is due to Zisman.^{15,16} The critical surface tension γ_c has therefore been taken as an approximate measure of the surface free energy γ_s of the solid. It should be noted, however, that the precise value of γ_c is generally dependent on the particular series of liquids used to determine the contact angle.

The critical surface tension concept would seem to indicate that a paint with surface tension less than the critical surface tension would be necessary to achieve good substrate wetting. In practice, it is found that good wetting and adhesion can occur with contact angles above 0° . In general, a low paint surface tension and, therefore, a low contact angle is desirable. Part of the problem with the critical surface tension concept is that different series of test liquids can extrapolate to different critical surface tensions for the same surface. A series of polar hydrogen bonding liquids such as alcohols give a lower γ_c than simple hydrocarbons, which interact less strongly with the same surface (Figure 16).¹⁷

Polyolefins and fluorocarbon polymers have low values of γ_c and are said to have low energy surfaces; these materials are difficult to wet and paint. Metals, ceramics, and polar polymers have high value of γ_c (high energy surfaces), can be readily wet by many paints, and exhibit good adhesion. Data on surface tensions of some typical solvents commonly used in coatings are shown in Table 2. In Table 3 are the surface tensions of some resins and additives used in coating formulations.

A dramatic example of the importance of wetting is provided by experiments with an epoxy resin and polyethylene.¹⁸ The adhesion is low (if any) when uncured epoxy is poured onto a polyethylene surface and then allowed to cure; however, if the polyethylene is melted and then applied to a surface of cured epoxy, the adhesion is much stronger. In the first case, a high surface energy liquid, e.g., epoxy, will not wet a low surface energy solid, e.g., polyethylene, with low critical surface tension. In the second case, wetting is favored because the liquid polyethylene is of lower surface energy than the solid epoxy. This demonstration is particularly significant because molten polyethylene has a high viscosity, typically about 10^3 Pa.s, compared to liquid epoxy, which has a viscosity of about 1 Pa.s. Apparently, viscosity is not important in this

instance when sufficient time is allowed for good wetting to take place.

Zisman plots are not without other drawbacks. Wu¹⁹ and others have pointed out that critical surface tensions often are low compared to surface tensions determined by extrapolation of melt or solution polymer data. Methods to treat contact angle data which are especially suitable for coatings and adhesives have been developed. In the Owens²⁰ procedure, the contact angles of at least two pure liquids, typically water and methylene iodide, are determined on the surface of interest. The surface tension is regarded as being composed of two contributions, dispersion and polar, such that

$$\gamma_1 = \gamma_1^d + \gamma_1^p$$

where γ_1 is the surface tension and γ_1^d and γ_1^p are its dispersion and polar components, respectively. The contact angle is related to the surface tension by the equation.

$$\gamma(1 + \cos \theta)/2 = (\gamma_1^d \gamma_2^d)^{1/2} + (\gamma_1^p \gamma_2^p)^{1/2}$$

Where γ_1 is the surface tension of the liquid and γ_2 is the surface tension of the solid. The results, using this equation, are generally in reasonable agreement with results obtained by other methods. In addition to contact angle measurements, standard wettability tests which are quick, robust, and easy to interpret have been developed.

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Canada melt flow test See **test, Canadian melt flow**.

can, beverage See **bottle; container; packaging, beverage-can**.

candela The luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian. See **geometric steradian; luminous flux; measurement; radiation, monochromatic**.

canopy 1. An ornamental rooflike structure that includes transparent or translucent plastic enclosures in shapes such as blisters, corrugations, and ribbing. See **building and construction market**. Canopies are transparent enclosures over an airplane cockpit. See **injection-molding aircraft canopy; transparent**. 2. The lifting or supporting surface of a parachute; usually made of woven nylon fibers and nylon major support cords.

canopy, rain-forest Small to very large enclosures where people or vegetation exist in a controlled atmosphere. Transparent large plastic panels are usually used supported by geometric reinforced plastic frames. See **rain erosion; reinforced plastic; transparent plastic**.

cantilever beam See **flexural testing; test, deflection temperature under load**.

cantilever, snap-fit See **design, snap-fit**.

cantilever, spring See **design, spring**.

canvas See **fabric, canvas**.

capacitance See **electrical capacitance**.

capacitor coating See **parylene plastic**.

capacity overhead rate See **business bookkeeping; capital equipment investment; economic evaluation; production capacity overhead rate**.

capillarity The attraction between molecules, similar to surface tension, that results in the rise of a liquid in small tubes or fibers, as can occur in filled compounds or reinforced plastics. See **condensation, capillary; drying, capillarity; rheometer, capillary; viscometer, capillary**.

capillary attraction The force of adhesion or bonding between a solid and a liquid in capillarity. See **adhesive**.
capital and inventors In 1871 Simon Ingersoll, an inventor with many patents, including rock-drill mining patents, considered himself a pure inventor who was part of a necessary equation for the advancement of technology. He wrote that to put over a new thing in the interest of the human race, it is necessary for some individuals to go "crazy" over a subject. It is equally important that (usually) someone else should furnish the money. Thus, this combination of a crazy inventor and capital equals the elements necessary to success.

capital equipment investment When a plant is to purchase equipment, a buy, loan, or lease can be used. Many factors influence the final decision, such as new equipment that processes materials at a faster rate than the old equipment did. If cash is used to purchase faster equipment, then additional cash will be required to purchase

more material, possibly more handling equipment, storage facilities for materials and products, and so on. Determining the true cost of each investment is based on developing the proper comparisons. If the comparison is based on total costs, then the usual way to go is cash. If cash is not available, then a loan is a consideration. Those with low tax rates or investment credit-absorption limitations could find leasing more attractive: (1) usually it is more costly to lease, (2) but cash outlay and down payment could be eliminated, (3) borrowing capacity increases, (4) it may be a way to gain additional assets, and (5) it shifts obsolescence from lessee to lessor. There are noneconomic factors to consider, and whatever action is taken, a risk factor is involved. See **business bookkeeping; economic evaluation; equipment; Euro and European Community; invest early; legal matter; warranty; machine aging; production capacity overhead rate; profit; sales investment turn**.

capital equipment investment tax credit A direct credit against the federal income tax that is allowed, generally, at 10% of the purchase cost with depreciable life greater than seven years.

capping See **coextrusion capping**.

caprolactam See **polycaprolactam plastic**.

capstan See **extruder wire and cable capstan**.

cap, tamper-proof See **mold, collapsible-core**.

captive processor See **processor, captive**.

car See **automobile, composite**.

carbazole White crystals, insoluble in water, obtained from ortho-amino-diphenyl and used in the production of polyvinyl carbazole plastics.

carbide A binary solid compound of carbon and another element. Familiar types include calcium, tungsten, silicon, boron, and iron. See **fiber, silicon carbide**.

carbon An element that provides the backbone for all organic polymers. It is a nonmetallic element occurring freely as a diamond, graphite, or coal. See **chemical composition and properties of plastic; element; mole**. Graphite is a crystalline form of carbon. Diamond is the densest crystalline form of carbon. See **mesophase**.

carbonaceous matter The component of a fuel, including solid waste, that consist of pure carbon or its compounds, usually associated with the residue of incineration. See **energy reclamation; incineration**.

carbon, activated A family of carbonaceous substances manufactured by processes that develop adsorptive properties. See **adsorption**.

carbon adsorption See **pollution; water**.

carbonated beverage bottle See **blow molding, stretched; bottle; Coca-Cola bottle**.

carbon atom linkage See **molecular structure configuration**.

carbon black A black colloidal carbon filler made by the partial combustion or thermal cracking of natural gas, oil, or other hydrocarbon. Depending on the starting material and method of manufacture, different forms with dif-