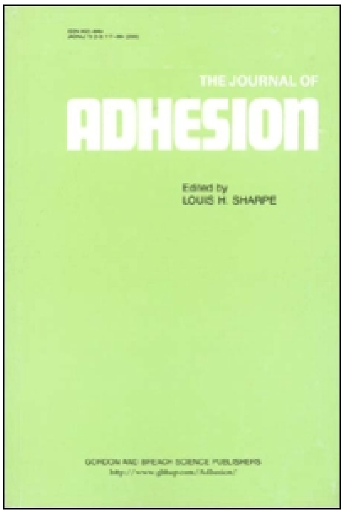

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Application of the Critical Surface Tension Concept to Items in Our Everyday Life†

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INTRODUCTION

One form of tribute to a scientist is the utilization of his work to advance technology. This review is to cite the application of Zisman's work to what are perhaps some unusual, or at least unfamiliar, technologies—dental restoratives, hair treatment, shaving and the processing of wastes. I have singled out these few because of personal involvement and recognition of the large contribution of Zisman and co-workers in their advancement and understanding. This, then, is a narrow and personal review of the scientific contributions of William A. Zisman.

ADHESIVE DENTAL RESTORATIVES

The requirements for the application and performance of adhesive dental restoratives impose greater challenge and constraints to the surface and adhesion scientist than for other, more familiar adhesive applications. Certainly, in no other technology is the designer of an adhesive joint similarly restricted to a medically acceptable, low temperature and fast setting, high strength adhesive which at the time of application and over the long term

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must be resistant to water and the mechanical stresses of mastication in an *in vivo* environment.

A few aspects of the development of adhesive dental restoratives bear review; their details have been published.[1, 2] Some of the contributions of Zisman and co-workers to the understanding of this field must be highlighted.

In order to achieve an adhesive bond to either tooth dentin or enamel: the tooth surface has to be wetted by the adhesive; suitable bonding established; and the *in vivo* water film displaced. These points are not mutually exclusive.

The wetting of tooth surface, or of the condensed water film on the surface, is similar to the wetting of condensed water films on glass or other supposedly high energy surfaces [3, 4] or of the surface of hydrated keratin, which is discussed in a later section below. The critical surface tension for wetting (γ_c) tooth substance is of the order of 25 to 30 dynes/cm, depending on the relative humidity (rh) and whether a dentin or enamel surface is involved.[2] This is provided, of course, H-bonding liquids are not used to determine γ_c;[5] the contact angle of a polyethylene glycol (γ_L = 44 dynes/cm) was near zero on a single crystal of hydroxyapatite, the mineral substance of teeth (cited in ref. 2).

The dependence of the γ_c of dentin and enamel on rh was also interpreted as consistent with the view that the surface of tooth tissue is rich in hydroxyl groups and/or firmly adsorbed water.[2] It is difficult to displace water from tooth surfaces; the displacement, as for other surfaces, has been related to Zisman's teachings regarding initial spreading coefficient, S_{ba}, and the relation between S_{ba} and the boiling point and solubility in water of the displacing liquid.[6] Liquids which displace water from dentin and enamel surfaces have the required high value of S_{ba} against water[6] and, interestingly, a large shift in the —OH stretching frequency in the ir spectrum when mixed with powdered hydroxyapatite, evidence of H-bonding.[2]

THE CRITICAL SURFACE TENSION OF HAIR

The application of fixative cosmetics to hair keratin, or the spreading of cosmetics or medicaments on skin keratin, would be expected to follow the same trends and principles as for other surfaces. However, whereas the critical surface tension ranges from 32 to 43 dynes/cm for a homologous series of polyamides,[7] γ_c of keratin was reported to be 27 dynes/cm for human hair and skin.[8, 9] The low value is not consistent with observations of wetting and spreading of various liquids on hair masses and difficult to reconcile with the now well-established correlations between γ_c and chemical constitution from Zisman's work.[10]

A possible reconciliation of the apparent anomaly was suggested by work of Shafrin and Zisman[11] on the properties of water surfaces and the effects of adsorbed water on the spreading of organic liquids on glass[3] and later on other inorganic surfaces[4] at high rh. Their results led to a greater understanding of the surface chemistry of hair. The parallel to the discussion of surfaces of tooth substance will be evident.

Values of γ_c for human hair, determined with liquids chosen to avoid possible H or pi bonding to water,[5] were found to be a function of rh.[12] Untreated or chemically oxidized (bleached) hair equilibrated at different values of rh exhibited different values of γ_c. For degreased fibers, γ_c ranged from 34 to 25 dynes/cm, for hair bleached with alkaline H_2O_2 γ_c ranged from 35 to 29 dynes/cm, over a range of rh of from 1 to 95%. For all samples, the value of γ_c fell rapidly with rh and reached a low limiting value at $< \sim 30\%$.

The low values of γ_c for hair—and the consequential surface chemical properties—were attributed to an adsorbed film of water[12] similar to the findings for other, better characterized surfaces.[3, 4, 11]

SHAVING

The shaving or mechanical cutting of human beard (or axial or limb) hair, unlike the discussion above, is not related to wetting and spreading. Cutting of hair, and particularly the almost effortless shaving introduced in 1959 and now commonplace, is rather related to sliding friction of hair on a thin polymer film adherent to the blade edge facets. (However, judging from the patent literature cited below, this is not the only factor.)

Zisman's teachings are again applicable; he and co-workers many years ago related coefficients of friction for sliding on thin polymer films and on fatty acid monolayers to surface chemical constitution.[13, 14] Not unexpectedly, low surface energy correlates with low coefficients of friction,[13] as an oversimplified summary. Surprisingly, however, not all low surface energy polymers—nor all low friction polymers—are useable as coatings on razor blades to achieve the easy shaving effect. For example, some siloxane polymers,[15] polytetrafluoroethylene[16] and polyethylene[17] have been reported as particularly effective. Of the three, perhaps the efficacy of polyethylene in producing the enhanced shave effect was the surprise. Early results of measurements of sliding friction of Zisman *et al.*[13] for bulk polyethylene showed relatively high coefficients of friction ($\mu_K \sim 0{\cdot}1$) compared to lower values for the siloxane polymers and polytetrafluoroethylene ($\mu_K < \sim 0{\cdot}05$). However, the low coefficient of sliding friction on high density polyethylene was observed ($\mu_K < \sim 0{\cdot}05$)[17] and later confirmed by

Bowers and Zisman.[18] Also, the dependence on the crystallinity (or density) of polyethylene[19] was confirmed[18] for bulk thicknesses and thin films on a hard backing.[17, 19]

The significance of all this is that early results from the Naval Research Laboratory[13] did not or could not explain findings of 10 years hence.[17] That is, judged from the results of 1953, high density polyethylene should not have had frictional properties similar to its fully fluorinated analog. Reexamination of the problem on a broader scale, i.e., better recognition of the crystallinity of the polyethylene used, fit the apparent anomaly within the correlations of surface chemical behavior and chemical constitution developed over the years by Zisman and co-workers. To his credit, Dr. Zisman reinvestigated his own findings and did not suffer an apparent anomaly.

THE SEPARATION OF WASTE PLASTICS

Recently, I found Zisman's teachings contributing to yet another unusual technology—the separation of waste plastics.

Certain industrial wastes contain mixtures of two or more types of plastics, for example cellulose acetate and poly(ethylene terephthalate) films left from the recovery of Ag from waste photographic and x-ray film and polyethylene and poly(vinylchloride) from the recovery of Cu from scrap wire. The plastics must be separated if they are to be reused; mixed plastics are usually weak and "cheesey" when moulded or extruded.[20]

Different types of plastics often differ in density so conceivably mixtures could be separated by float-sink in a liquid media of controlled density. However, plastics often contain mineral fillers or have been foamed; both processes alter the density and thus interfere with a sink-float separation. Also, waste plastics may be dirty and not wet by the sink-float fluid.

Then seemingly a curious thing happened. When trying to separate polyethylene (PE), density 0·92 g/cm^3, from poly(vinylchloride) (PVC), density 1·3 g/cm^3, Sheng[21] observed that when using water containing wetting agents, the PVC floated and the PE sank. The explanation for this is clearer after briefly reviewing how the phenomenon is taken advantage of in a process recently developed in Japan[22] for the recovery of individual plastics by type from mixed plastic waste (independent of Sheng).

Binary mixtures of waste plastics, pieces of the order of ½ to 1 cm in size, are mixed with an aqueous solution of wetting agent and air bubbles are introduced, which appear to adhere preferentially to one of the plastics. The developer likens the process to the froth flotation of inorganic minerals, although it is difficult to invoke concepts of specific electrical and adsorptive surface forces in an explanation of the behaviour of low surface energy plastics, as is done with high surface energy minerals. The plastic mixture is separated in that the higher density plastic can be preferentially floated or sunk, free of the other, depending on the particular mixture and choice of wetting agent.[22]

Small solid particles placed on a liquid surface, such that the density of the plastic is greater than the density of the liquid, will float when sustained by an upward force due to the surface tension of the liquid. However, for particles small enough that the sustaining force is of the same order of magnitude as the gravitational force, the particles will sink at $\gamma_L = \gamma_c$.[8] Apparently, the Japanese process can use large particles because of the introduction of air bubbles. The developers point out that the surface tension of the liquid medium is adjusted so that the contact angle is zero on one of the plastics to be separated.[22] The separations are quite good, seemingly better than could be achieved by say just float-sink in water, judging from the mechanical and chemical properties of the recovered plastics.

CONCLUSION

I have had the pleasure of being associated with each of the technological developments reviewed above. More important, I have had the privilege of benefiting from the teachings, counsel and friendship of Bill Zisman through these and other developments. I am proud to add my praise and thanks on this occasion.

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