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A PRACTICAL APPROACH TO CHOOSING A SUBSTITUTE SOLVENT

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INTRODUCTION

Organic solvents have a multitude of uses in industrial processes, and, although there is some progress being made in replacing them with aqueous systems, many applications still require them. Many cleaning operations which require merely removal of light soils and easily emulsified oil or grease have been changed to aqueous systems with excellent results. Other applications, such as paint removal, cleaning of easily corrodible metal surfaces, removing polymer coatings, or baked on carbon, still may require application of an aggressive solvent. This paper will focus on coating removal, or paint stripping, and consider several instances where substitutes were chosen, and attempt to explain why (or why not) these substitutes performed well.

A major use of organic solvents is in the formulation of solvent coatings such as paints, enamels, varnishes, and lacquers. This is an extremely broad and specialized field, and will not be covered in this brief discussion. Instead, we will discuss the other end of the spectrum, that is, removing coatings which have reached the end of their useful life. The techniques for choosing solvents for coating removers can follow almost the same rules used to formulate them, except that while the resins used to formulate a coating are soluble in the proper solvent mixes, many coatings cure or crosslink after application and become insoluble, and merely swell or soften. Indeed, complete dissolution of the coating to be removed is undesirable, since a softened coating may be removed in large pieces, instead of as a viscous solution.

A brief outline of progress in solvent selection indicates that the earliest discovery that solvent mixtures were more effective than pure solvents was made by paint and varnish formulators. As knowledge advanced, the Edisonian approach of trial and error was replaced by reasoning; if one had a clue about the chemical structure of both the resins being dissolved, and of a group of available solvents, then trial and error could be reduced. Others postulated that physico-chemical parameters of both the solvents and resins or other solutes could be measured and described mathematically using solution theory. Modern solution theory relies heavily on work done 40 or more years ago by Hildebrand[1] and expanded upon by Hansen[2]. Hansen proposed that there were three contributors to the solubility parameter as developed by Hildebrand which he designated S_d, S_p, and S_h, each contributing in its own way to the overall solubility of a compound, and that a close numerical match (about 1 or 2 Hildebrand(H)) is required for mutual solubility of two compounds. S_d quantifies the dispersion or van der Waals intermolecular forces; these are the primary forces at work in hydrocarbons. S_p is a polar component common to acids, alcohols, etc. S_h is the hydrogen bonding parameter which designates the bond between hydrogen and two unshared electrons of another molecule. There are several tables of these values available, notably the Solvent Properties chart listing over 200 solvents prepared by Dr. Tom Marquis and published by Texaco Chemical Company, (now Huntsman Corporation). Huntsman Corporation has also developed a computer program which will calculate the solubility parameter of mixtures of solvents. Others have both tables and computer solvent selection programs available today[3], although some programs concentrate more on such factors as evaporation rate, smog formation, and flash points.

RREL and the U.S. Air Force recently funded an extensive assessment of pollution prevention opportunities at Tinker Air Force Base (TAFB), Oklahoma. Among the processes evaluated by the contractor, Battelle, were a number of depainting and degreasing operations where either toxic, flammable, or ozone depleting solvents were used. One of these was a depainting operation where aircraft radomes were depainted by showering them with methyl ethyl ketone (MEK).

The radomes to be depainted at TAFB had three coats of paint; an epoxy primer, a urethane rain erosion layer, then a low visibility topcoat. When time came to overhaul an aircraft, the radomes were removed, the coatings were scored, and the radome placed under a shower of MEK until the coating bubbled and could be squegeed off; the operation typically takes 1 1/2 to 3 hours. Because of the flammability, volatility, and toxicity of MEK, the shower was enclosed in a large closed booth with forced ventilation. During the process, MEK vapors were discharged to the atmosphere, and about 50,000 pounds were lost in 1992. One of the coauthors, Mr. Johnny Springer, was Project Officer on a task to determine if mixture of solvents would perform almost as well as MEK, be less volatile, have a higher flash point, and be less toxic. After looking through a table of solubility parameters, it appeared that a low volatility, non toxic solvent such as propylene carbonate (PC) blended with others to match the S_o, might make a candidate replacement solvent. Dr. Marquis agreed to try to develop a substitute mixture having the requisite characteristics, as he thought a single solvent would not be effective. Development of these formulations and some guidance on developing new ones are the subject of this paper.

METHODOLOGY

Using the Hildebrand solubility parameter of MEK as a rough starting point, Dr. Marquis made up several blends of solvents for laboratory testing. All of the blends contained propylene carbonate and N-methyl pyrrolidone (NMP) and at least one other solvent. The combinations were not chosen on their removal efficiency alone; vapor pressure (a large contributor to evaporation rate), flash point, and toxicity were also considered. Small sections of a condemned B-52 radome were immersed in the solvent blends in open beakers and compared to MEK, however it was noted that the volatile MEK evaporated rapidly, which was overcome by enclosing those beakers in polyethylene bags. Table 1 lists the time required for the paint to completely Bubble so that it could be easily wiped off. MEK took up to 12 times as long to bubble the coatings in this test as the mixtures did. This did not compare to the experience of the operators of the depainting operation at TAFB; their experience with the shower head arrangement indicated that complete removal of the paint usually occurred in less than three hours.

TABLE 1

Solvent	S_d	S_p	S_h	Strip Time Hours	Composition by Weight (%) PC NMP DBE
MEK Dry	7.8	4.4	2.5	24	
Blend 1	8.9	5.6	3.5	4	33.33% each
Blend 2	8.9	5.7	3.5	2	25 50 25
Blend 3	8.5	3.8	4.2	4	15 15 40 DPM 15 MIAK 15

MEK - methyl ethyl ketone; PC - propylene carbonate; NMP - N-methyl-2-pyrrolidone;DBE - Dibasic esters (Du Pont) (mixture of dimethyl esters of succinic, glutaric, and adipic acids);DPM - Dipropylene glycol monomethyl ether;MIAK - Methyl isoamyl ketone

Looking at the solubility parameters of the blends indicates that they were all fairly similar to those of MEK, and therefore should not differ too greatly in solvent activity. Questioning of the engineer in charge of the TAFB operation revealed that the removal time with MEK decreased after the first run or so, and that he suspected water absorbtion from the air could be the reason. From this information, the contract laboratory reasoned that enclosing the beakers was a mistake, and found that open beakers of MEK performed better. They then found that adding 12.5% of water to the MEK yielded bubbling times of 30 minutes. This contradiction of conventional wisdom was not apparent at first, since one would think that water would detract from, rather than augment, removal efficiency. An explanation of this was sought by reevaluation of the MEK solubility parameters, especially S_h. Looking again at Table 1, S_h of MEK is 2.5, only 1 Hildebrand (H) lower than Blend 2, the best of the three tested. In general a match within 1 H is considered adequate for solvent matching, but knowing the effect of water, the strongest hydrogen bonder, on the process, the effect on this parameter was calculated.

Solvent blend 2 in Table 1 is clearly the best paint stripper of the three blended solvents. Its hydrogen bonding parameter is 3.5 compared to 2.5 for MEK, and S_p at 5.7 is clearly higher than MEKs 4.4 H. It is then quite likely that an important part of this blends effectiveness is the hydrogen bonding ability of one or more of its components. NMP is hygroscopic, that is, it readily absorbs water out of the air. Blend 2, having 50% NMP, quite likely absorbed water during the time it was in the beaker with the radome section. The calculated S_h of both MEK and NMP are increasing as water is added, and at 12.5% water, MEKs S_h is about 4.3H; Blend 2 only requires 4% water reach 4.3H. This may partially explain why MEK/water is an effective stripper for this particular coating.

Solvent blends 1 and 3 are apparently affected by S_p and a third factor, dielectric constant, closely related to it. An attempt to incorporate this factor into an overall equation is underway, and will be the subject of a subsequent paper.

What's happening? Why does Blend 2 work almost as well as MEK/water? Why doesn't plain water remove the coating? While there is no trite answer to the questions, an effective remover/stripper must have the following characteristics:

A. Ability to diffuse into the film. Only one of the components of a blend may do this alone, but it may carry the others with it, as diffusion implies solubility, which means that polymer chains are separated[4] by solvent.

B. The proper solvent power to move coating molecules apart so that the film is softened and/or swelled. In this, and in (A.) above, the solvent must have at least one parameter which matches the coating film. For example, a styrene/butadiene rubber will hardly be affected by MEK but will swell considerably in hydrocarbons such as toluene. This is easily determined by experimentation, but also by looking at the solvent properties chart, and a list of polymer solubility parameters[5,6]. In this case, should the solvent be too effective and make the surface sticky, adding a poor or moderately hydrogen bonding solvent could produce a good swelling or removal agent.

C. Adhesion of a coating to a substrate can occur in several ways. In the case of the radome example above, it was apparently largely through hydrogen bonding, and increasing the hydrogen bonding parameter of the solvent with the addition of water allowed water to occupy sites at the polymer/substrate interface, weakening the polymer/substrate bond. Conversely, using toluene to remove a hydrocarbon coating may work, but if not crosslinked, the coating might dissolve completely, making a viscous solution almost as difficult to remove as the coating. This might be overcome by adding another component which is a moderate hydrogen bonder which would keep the resin from going completely into solution.

D. When the coating polymer is polar, as polyurethanes are known to be, a solvent of high dielectric constant may aid in separating charged areas, thus making space for other solvents to soften the film.

If a table of polymer solubility parameters includes the one you wish to strip, so much the better, but if not, a practical technique for developing a stripper/ remover would be to find one that does the job, however volatile, toxic, or odoriferous it may be, and try to find its solubility parameters in the literature. From this point, one may develop a solvent blend which closely matches these parameters.

We are continuing work on finding solvent substitutes; our next task, which is to the reporting stage, is finding a blend which eliminates NMP, as it has recently come under suspicion of being a mutagen. Findings from the MEK/NMP/PC study above will help in this task. Our next planned project is to find a substitute for the phenol/methylene chloride stripper used on complete aircraft. This might prove to be much more difficult than stripping a relatively small, smooth surfaced radome. There are problems of corrosion, volume of solvent, and overall cost, since active solvents are more expensive.

REFERENCES

1. Hildebrand, J.H., Scott R.L. The Solubility of Non Electrolytes Reinhold, New York, 1950.

2. Hansen, H.J. J. Paint Technol. (1967) 40, 197.

3. In addition to Texaco-Huntsman, Dow Chemical Co., Shell, Arco, BP, Eastman, and EXXON have computer programs for choosing solvents.

4. Hildebrand reasoned that the energy required to separate two molecules could be measured by the heat of vaporization. While this measurement is feasible for small molecules, polymers usually decompose before they vaporize, so their solubility parameters are measured indirectly, by finding solvents which will dissolve or soften them. The solubility parameters of the solvents are then used to estimate that of the polymer.

5. Brandrup, J., Immergut E.H. Polymer Handbook Wiley Interscience, New York 1989 p. VIII 519.

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