17 Applications — Safety and Environment

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ABSTRACT

Hansen solubility parameters (HSP) can be used to gain insight into many safety and environmental issues. These include substitution to more desirable materials, products, and processes, where a listing of solvents having HSP similarity to the one(s) to be substituted provides an overview of the potential choices for improvement. Selection of suitable chemical protective clothing can be improved by considering HSP correlations of breakthrough time. Evaluating risks for inadvertent chemical uptake in plastic can be helped by HSP correlations of chemical resistance and/or permeation phenomena. Similarity of HSP suggests which chemicals are most likely to be rapidly absorbed into given plastic types. These same approaches can be used to evaluate the potential for uptake of chemicals through human skin.

INTRODUCTION

Many organic materials are potential safety hazards. They can also be harmful to the environment. Unfortunately, it is often a matter of experience before the risks are uncovered because of damage being done. Thus, over the years, there have been a series of substitutions with or without the aid of HSP to eliminate or to at least reduce such problems. An example is the lack of emphasis on the use of some ethylene glycol ethers as solvents because of their teratogenic effects, whereas they were used in massive quantities earlier. The problem of replacing ozone-depleting chemicals is a case involving the external environment. This is discussed a great deal in Chapter 11. Other large-scale substitutions can also be cited where HSP can aid, but a list of this type is not the purpose of this chapter. The emphasis here is on the use of sound formulating principles to reduce the potential hazard in terms of reformulation or substitution. When a satisfactory substitution cannot be found, personal protection of one type or another may be required. Here, again, HSP can help.

Evaluating other forms of environmental risks can be aided by using HSP. An example is the occasional misuse of plastic containers normally used for soft drinks to store chemicals such as herbicides and pesticides. These are likely to diffuse into the plastic container wall itself, making customary washing insufficient. HSP can indicate which chemicals can do this, thus providing information on the means to improve handling of the problem. This type of information can be generated for any polymer where HSP correlations of chemical resistance, weight gain, etc., can be generated.

All of these situations are discussed in more detail in the following.

SUBSTITUTION

Substitution involves the replacement of a potentially dangerous process or chemical with a new process or chemical having less hazardous properties. The hazards can be judged using accepted approaches — for example, labeling requirements, toxicology assessments, biodegradability, and physical properties for the chemical or products. The volatility of products is also a significant factor with lower volatility being preferred due to reduced workplace concentrations and reduced replacement requirements for cleaners and the like which often recirculate in nearly closed systems. On the other hand, the problem should not just be transferred from the air exhaust system to the sewer.

The use of technologies involving water or mechanical methods, such as mechanical joints rather than the use of solvents, are preferred. Examples of preferred coatings technologies are the use of powders which flow at higher temperatures or polymerization by radiation, both of which use solvent-free base products to provide the coating. Other product types which may be targeted include cutting fluids, cleaners of various types, adhesives, sealers, and fillers.

In general, one primarily wishes to substitute for

- Carcinogens or suspected carcinogens
- Substances with risk phrases for being very toxic, toxic, allergenic, carcinogenic, teratogenic, mutagenic, or causing cumulative or irreversible effects
- Substances with moderate or serious aquatic toxicity
- Nonbiodegradable substances
- Substances with high predicted aquatic effects — for example, chemicals which preferentially distribute to a nonaqueous phase to a very high degree

Efforts should be made to develop products with the lowest possible hazard. Those who have read the earlier chapters in this book will immediately recognize HSP as a tool to aid in the substitution and systematic formulation for reduced safety and environmental risks. A key element in this is a listing of solvents where those most resembling the candidate for substitution are at the top of the list. The program described in Chapter 1 can do this by entering the HSP for the solvent to be replaced and requesting a listing with those solvents most similar to it (i.e., the lowest RED numbers as defined in Chapter 1, Equations 1.10) at the top of the list. One must then sort through these potential replacement candidates using other information to arrive at a better alternative.

It is clear that much more data than HSP are required to make the desired substitutions. However, a further discussion of this is beyond the scope of this chapter, which emphasizes HSP only. The currently used HSP techniques and correlations can aid in some aspects of substitution, and it is anticipated that future correlations will help in this endeavor. Many cases of substitutions in practice have been listed by Goldschmidt,[1] Olsen,[2] Soerensen and Petersen,[3] and Filskov et al.[4] A long list of references for the Danish experience with occupational risks and solutions is given by Soerensen and Petersen.[3]

ALTERNATIVE SYSTEMS

Alternative systems with less solvent or no solvent have been focused on by the coatings and printing ink industries for many years. Examples of such systems are coatings with higher solids, radiation-curable inks and coatings, powder coatings, electrodeposition coatings, and other water-reducible products. It might appear that solvent technology and use of HSP will not be as important as it has been in the past. This is not the case, however, as demonstrated in earlier chapters. For example, HSP principles can be used to aid in improved stability and adhesion, to predict polymer/filler interactions, to improve barrier polymers, and to aid in understanding some biological phenomena.

The use of solvents in alternative coatings systems has been the topic of several previous publications by the author.[5–8] Some general principles of solvent selection have been discussed in Chapter 8 and earlier,[9] as well as elsewhere more recently.[10]

SOLVENT FORMULATION AND PERSONAL PROTECTION FOR LEAST RISK

Solubility parameter principles have been used in formulating alternative, low VOC (volatile organic compound) products. A number of the general formulation principles can be briefly stated for the sake of completeness. These include the following:

1. Solvents with lower viscosity most often lead to polymer solutions with lower viscosity. Such a change allows the use of higher solids at the original viscosity. However, these may evaporate more rapidly and can be expected to have a lower flash point.
2. Solvents with linear and smaller structures diffuse more rapidly than those with branched and larger structures. Inclusion of slower evaporating, more linear solvents can hasten the through-drying of a coating.
3. Two (or more) mixed solvents with lower labeling requirements may be able to replace a single solvent. HSP can be used in this type of endeavor.
4. The surface tension of water-reducible coatings can often be significantly reduced by relatively small additions of ethanol or other alcohol-type solvent. These can, of course, also be used in conjunction with other surface active materials.

Materials with least potential risk are to be used in the Nordic countries wherever possible. The risk must be indicated by the seller/producer in terms of a labeling code. The risk can then be assessed by users or, perhaps more specifically, by primarily professional users. Such labeling is required on paints, printing inks, cleaners, or for any product containing significant amounts of solvent or hazardous chemical. The labeling code dictates the personal protection required for the product, depending on the way it is used. Spraying product in a smaller room with limited ventilation requires much more protection than applying paint with a brush outdoors. Tables have been published which give the protection required (gloves, dust mask, fresh air mask, body suit, etc.) for a given set of application conditions for a wide variety of products from paints and printing inks through cleaners.[11] A key element in these tables is the labeling code developed in Denmark according to the MAL (in Danish: Maletekniske Arbejshygieniske Luftbehov) system. For present purposes, this is translated as the FAN (fresh air number). Higher MAL/FAN dictate that more extensive personal protection is required.

THE DANISH MAL SYSTEM — THE FAN[12]

As indicated previously, the quality of the working environment must be considered in all cases where organic solvents are being used. The Danish MAL system or other labeling system can be systematically used for this purpose. The Danish MAL reflects the cubic meters of fresh air required for ventilation of 1 l of product to below the threshold limit value (TLV). This number is modified by a constant, depending on the evaporation rate (or vapor pressure). Higher evaporation rates imply greater hazard, so the multiplier is larger.

The concept behind the MAL system can be better understood in English by translating the MAL number as the FAN. Other numbers in addition to the TLV/GV/OEL (occupational exposure limit) and FAN have been generated to help evaluate risks by inclusion of evaporation rate/vapor pressure considerations. The vapor pressure divided by the TLV is called the *vapor hazard ratio* (VHR) and the actual calculated vapor composition (using activity coefficients) divided by the TLV has been called *SUBFAC*. A Danish publication comparing several of these is available.[4] To demonstrate the principle, the simple MAL = FAN has been tabulated in Table 17.1 for several solvents.

TABLE 17.1
Fresh Air Numbers (FAN/MAL) for Selected Solvents from the Danish MAL Labeling System[a]

FAN/MAL	Solvent	FAN/MAL	Solvent
1400	Chloroform	20	*n*-Propanol
1100	Tetrachloromethane	19	Propylene glycol monomethyl ether acetate
880	Benzene	17	Propyl acetate
110	Dichloromethane	15	Propylene glycol monopropyl ether
88	Trichloroethylene	14	Mineral spirits/white spirit
78	*n*-Hexane	14	Butyl acetates
74	Toluene	13	Ethyl acetate
58	C9 Aromatics	13	Cyclohexane
54	Methanol	13	Benzin/petroleum ether (as heptane)
48	Methyl ethyl ketone	12	Heptane
46	Xylene	7	Ethanol
29	2-Propanol	6	Propylene glycol monobutyl ether
28	Propylene glycol monomethyl ether	5	Dipropylene glycol monomethyl ether
26	1,1,1-Trichloroethane	4[b]	DBE (dibasic esters)
25	C>9 Aromatics	0	Ethylene glycol
24	Tetrahydrofurane	0	Propylene glycol
23	Acetone		

[a] These numbers are developed primarily with regard to health hazards from vapors. The second number in the FAN code is added for hazard for skin contact, eye contact, respiratory system contact, and/or ingestion. In addition to these, the European Union requires use of Xi, Xn, C, T, etc. Several of the solvents require such labeling as well. One must also consider R (risk) and S (protective measure) labeling requirements.
[b] Estimated from composition of the mixed solvent.[15]

Each product containing solvent is assigned a two-digit number to place it into a potential hazard category. This number is a summation of the hazards possible for the components which are considered potentially hazardous. The first number relates to the potential hazard from the vapors and will vary from 00 through 0, 1, 2, 3, 4, 5, to 6 as the potential hazard increases. The second number varies similarly and relates to the potential hazard from direct contact with the skin, eyes, breathing system, and by ingestion. This second number will not be less than 1 if organic solvents are included in the product in significant amounts. The following is a list of several solvents which are considered less desirable, based on this second number being 3 (or higher for higher concentrations in some cases): Toluene and Xylene at >10%, all common ethylene glycol based ethers and their acetates (including diethylene glycol monobutyl ether, for example), terpenes, monomers at rather low concentrations, amines at moderate concentrations, and the most common chlorinated solvents. A "3" in this category places the protection required in a significantly higher category with requirements for gloves as a minimum and frequently fresh air masks as well.

As indicated, a two-digit MAL code defines which safety precautions are required for each of a large number of processing operations and conditions, including interior and exterior painting and gluing, whether or not large surfaces are involved, the quality of ventilation provided, surface preparation, painting of ships, larger construction sites, each of the printing processes, and industrial coating (spray boxes, cabinets, etc.).[11] The protective measure required may be a face guard, eye protection, a dust mask, a gas filter mask, a combination filter mask, a fresh air supplied mask, or a body suit, in order of increasing requirements.

Examples of complete labeling of products and solvents are beyond the scope of this chapter. The purpose of the discussion is to suggest that possible substituting solvents can be listed, such as in Table 17.1, in an attempt to find a substitute with a lower labeling requirement.

Systematic consideration of labeling requirements is becoming a significant parameter in commercial applications of solvents and products containing solvents. This is happening all over the world, both with regard to worker safety as well as to the external environment. Such a procedure has been used to arrive at optimum commercially useful solvent compositions with the lowest possible risk for workers in the serigraphic printing industry as described in Danish patents DK 153797B (1989) and DK 160883 (1991) which correspond to European patents EP 0 205 505 B1 and EP 0 270 654 B[13,14] The preferred compositions reduce the MAL number to a minimum and also consider lowest possible internationally required labels as a requirement. The low label requirements of DBE (dibasic esters) have been emphasized in comparison with other solvents.[15] Systematic solvent selection procedures have also been strongly suggested for use in the selection of solvents for restoring older paintings.[16] This is discussed in Chapter 5.

SELECTION OF CHEMICAL PROTECTIVE CLOTHING

HSP correlations for barrier properties of some types of chemical protective clothing are given in Chapter 13, Table 13.1. These correlations are based on data presented by Forsberg and Kieth.[17] Other examples of HSP correlations of barrier properties of protective clothing are discussed in Chapter 13. Earlier publications also include HSP correlations of barrier properties of chemical protective clothing.[18–21]

The procedure for using these correlations requires knowledge of the HSP of the chemicals involved. These may be found in a suitable table or can be calculated according to the procedures outlined in Chapter 1. One then evaluates the RED number for the situation of interest. The RED number is discussed in Chapter 1 (Equation 1.10). If this number is less than 1, the system in not expected to be suitable for use. If the RED number is close to 1.0, there may be some doubt about the recommendation. RED numbers significantly greater than 1.0 can be considered for use. As discussed in Chapter 13, the molecular size of the chemical involved is important in these evaluations.

The major use of such correlations is to evaluate potential barrier types for chemicals where test results are not available. One can usually divide the results into groups of clearly not acceptable, questionable, and worthy of further consideration.

There have been recent attempts to improve on the direct correlation of breakthrough times and permeation rates with HSP by trying to estimate the solubility and diffusion coefficients separately using HSP.[22–25] These efforts have been discussed in Chapter 2 and Chapter 13.

UPTAKE OF CONTENTS BY A PLASTIC CONTAINER

Plastic containers have become increasingly popular in recent years. They have many advantages (which will not be discussed here), but there is also one disadvantage that HSP can shed more light on. This is the fact that plastic materials are able to absorb various liquids to some extent. The extent of absorption clearly depends on the HSP of the plastic used in the container compared with the HSP of the liquid which is in contact with it. Containers in contact with food have been tested well for suitability for this purpose, including barrier properties relative to the contents. This is not the point of the present discussion. A problem exists with the inadvertent storage of hazardous liquids in the plastic container prior to its expected recycling as a container for a food or beverage. Many types of liquids can be temporarily stored in such containers. Whereas the earlier glass or metal containers could not absorb potentially dangerous materials, a plastic container can do this. A simple washing operation cannot be expected to remove all of the absorbed material. Washing only removes what is on the surface or what can diffuse to the surface during the washing process, which presumably takes place at some higher temperature.

HSP concepts can focus attention on the types of chemicals that can absorb into a given type of plastic container. This is useful information in terms of what analyses should be performed prior to recycling. The principles discussed here can possibly contribute in other ways to improve the recycling process based on the increased level of knowledge. There may be other ways to reduce the problem.

SKIN PENETRATION

Human skin is a complicated system. Nevertheless, it has been possible to characterize some aspects of the behavior of human skin by HSP. The HSP found in a correlation of permeation rates of liquids in contact with viable skin[26] are similar to those found for the swelling of psoriasis scales.[27,28] This has been discussed in Chapter 15 in more detail, but also relates to worker safety. The HSP for these correlations are included in Chapter 13, Table 13.1 and Chapter 15, Table 15.1.

A skin penetration warning has been attached to many liquids taken up in the lists of limiting values for workplaces which are published in different countries. It was found earlier based on the HSP correlation with the swelling of psoriasis scales that this practice could be misleading, as HSP predicted many liquids without this warning also swelled psoriasis scales (keratin) and could therefore be expected to penetrate the skin.[27] The lack of a skin penetration warning for these liquids is partly attributable to the fact that this warning is based on experience. The bad experience giving the warning includes a combination of all effects, most notably the combination of dose and toxicity, rather than the potential dose effect only which is indicated by similarity of HSP. Earlier discussions also led to the impression that those involved in this area did not consider the swelling of psoriasis skin as having relevance to the permeation of living skin. The finding that comparable δ_P and δ_H are found from correlating the permeation rates of solvents through living skin is a new input into this discussion. It is recognized that the δ_D parameter is different, but reasons for this are not clear. An improved HSP correlation of the permeation rates of solvents through living skin based on a larger number of solvents than the 13 included in the work of Ursin et al.[26] is perhaps required to give improved predictions in marginal cases, i.e., those near the boundaries of the HSP sphere describing the situation. The size and shape of the penetrating liquid molecules must also be considered.

Predictions of the barrier properties of viable human skin should receive more attention. In addition, there is some discussion of the use of HSP in this respect in Chapter 15.

TRANSPORT PHENOMENA

Many chemicals have been the subject for concern in the past for various environmental reasons. Among these is the presence in artic regions of chemicals that do not readily break down. Some chlorinated materials, such as pentachlorophenol, have the ability to penetrate skin and wood, and to be transported by animals, birds, or aquatic species after they have taken them up. The HSP of given chemicals can give a clue as to whether or not they can follow the same pathways in the environment. An example is given in Table 17.2 where the HSP for tetrabromobisphenol A (TBBPA) are reported along with the similarity of these with other relevant materials.

TBBPA has a distance from Pentachlorophenol (PCP) of only 3.5 units. This is very close and means that where PCP is soluble, TBBPA will also be soluble.

TBBPA has a distance from the center of the spherical HSP correlation for Lignin solubility of only 6.8 units. Dividing this by the radius of the sphere to find the RED number (relative energy difference) shows that it is well within the solubility region with a RED of 0.5. TBBPA is readily soluble in lignin (wood).

TABLE 17.2
The Affinities of Tetrabromobisphenol A (TBBPA) for Selected Biological Materials

Material	δ_D	δ_P	δ_H	Ro	Dist. to TBBPA
TBBPA	20.2	9.1	13.8	—	0.0
Pentachlorophenol	21.5	6.9	12.8	—	3.5
Lignin solubility correlation	21.9	14.1	16.9	13.7	6.8 (RED = 0.50)
Rapid skin penetration correlation	17.6	12.5	11.0	5.0	6.5 (RED = 1.36)
Swelling of psoriasis scales correlation	24.6	11.9	12.9	19.0	9.3 (RED = 0.49)
Depot fat (37°C) total solubility	15.9	1.2	5.4	12.0	14.3 (RED) = 1.20
Blood serum	25.5	10.3	22.1	17.8	13.1 (RED = 0.73)

Note: Units are $MPa^{1/2}$.

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TBBPA has a distance from the center of the spherical correlation for rapid skin permeation of 6.5. This is just outside the region for rapid permeation, but means that permeation will certainly take place at a moderate rate. The size and shape of the molecule will dictate the rate of permeation, not the solubility relations.

TBBPA will readily absorb into the outer layer of the skin (keratin) here described by swelling of psoriasis scales. The rate of absorption is dictated by the size and shape of the molecule, and not by the solubility relations.

These data confirm that TBBPA is readily soluble where pentachlorophenol is soluble. If the chemical stability is comparable or better, then it can be presumed to appear at the same places if it gets into the environment. The same is true of related brominated compounds in general. Both pentachlorophenol and TBBPA can readily penetrate wood and wood products. They will also be readily taken up at lower concentrations without delay by human skin as shown by the correlations of rapid skin penetration and the swelling of psoriasis scales. Similar analyses can be done with other chemicals. HSP are available in Appendix Table A.1 for many phthalate plasticizers, mono 2-ethylhexyl phthalate, bisphenol A, *N*-methyl-2-pyrrolidone, and various glycol ethers based on ethylene oxide. In principle any compound of interest can be assigned HSP for use in predicting behavior in connection with a large number of environmental subjects.

The correlations of the solubility of depot fat at 37°C, the solubility of a protein (human blood serum), and swelling of keratin (psoriasis scales swelling) indicate that TBBPA prefers to reside in the nonfatty tissue, but that it will have some solubility in the fatty tissues as well.

The collection of chemicals in fatty tissue is another topic that could be explored. A simple rule of thumb is that lack of water solubility will encourage collection in the fatty tissues, but this could be given more precision with HSP. The major problem with this collection is that the central nervous system is almost completely fatty in nature, and an excess of foreign materials can short-circuit, misdirect, or stop messages, leading to memory problems, etc.

CONCLUSION

In conclusion, it can be noted that HSP provides a tool to aid in substitution and in systematic formulation of less hazardous products and processes. One can also use HSP to more rapidly arrive at an optimum choice of chemical protective clothing. HSP provides other insights with regard to uptake of undesirable chemicals in the human skin, in packaging materials, and perhaps even in a wide variety of other materials such as those found in nature.

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