

CHAPTER 1

INTRODUCTION

1.1 Overview

The solvent was added to paints to reduce the viscosity of the paint to meet application requirements.

The proper selection of solvent for polymer or resin is very important due to the fact that the inappropriate choice would result in coating film that is easier to scrap off (Sorawaree, 1996). The quality of film coating depends on solubility and evaporation of solvents. Serious problems can be generated by too fast or too low evaporation rate. In addition, the poor solubility of some solutes can cause precipitation of resins (Castells and Casella, 1987).

Solvent evaporation from coated films is a process influenced both by internal factors such as vapor pressure, heats of vaporization, solution activity coefficients, thermal conductivities and diffusivities, and by external factors such as the air flow velocity and direction, relative humidity, the temperature of the film and its surroundings. Therefore, the additives are used to dissolve the paints and adjust the viscosity to be for plastic printing (Castells and Casella, 1987).

Solubility of polymer and resin is dependent upon the solubility parameters, hydrogen bonding and dipole moment of the solvent. Solubility parameters are the most important property of all, followed by hydrogen bonding. Consequently, a material is insoluble or incompletely soluble in a solvent if its solubility parameters and hydrogen bonding properties fall

outside suitable region (ASTM D 3132, 1972).

In addition, the selection for the solvents to be suitable for polymer and resin in use, other aspects to be considered include working environment and the workers safety and health.

One of the major problems encountered is the fast evaporation rate of the thinner. Therefore, the main objective of this cooperative study is to find appropriate solvents with lower evaporation rate of the thinner while maintaining good viscosity and adhesion.

1.2 Principle for selecting materials

1.2.1 Classification of surface coating materials

The surface coating materials can be classified into three classes:

1.2.1.1 Paint including pigments, binder (vehicle), solvents and additives.

1.2.1.1.1 Pigment is used to provide or hide colors. A pigment can be an organic or inorganic compound.

1.2.1.1.2 Binder or vehicle is dispersed in the pigment and retain them on the plastic film surface after printing. The examples of the binder include drying oil, natural resin and synthetic resin.

1.2.1.1.3 Solvent is a liquid which adjusts viscosity for the ink and transfers the ink from the printing system to the substrate. The solvents are mostly organic compounds.

1.2.1.1.4 Additives are added in small quantity into the pigment to provide special properties such as drying agents, waxes, surfactants and antioxidizing agents (Geol *et al*, 2001).

1.2.1.2 Varnish is surface coating materials that consists of only binder.

1.2.1.3 Lacquer is a solution made by dissolving resin or binder with organic solvents.

1.2.2 Film formation

Film formation is the converting of surface coating materials to adhering film with durability. Film formation process consists of three steps:

1.2.2.1 Application

The application is the process to coat the material onto surface or reinforce the surface to form thin film. Application can be performed by brushing, rolling, dip coating or spraying.

1.2.2.2 Fixation

The fixation is the process to make the film strongly fixed, not to perform detachable from surface and without forming incomplete layers. For example, in the case of the coating materials with organic solvent, the film formation in the process of fixation can be achieved by evaporation of the solvent. For the coating material in the latex system, the step of fixation is performed by the evaporation of water.

1.2.2.3 Curing

The curing is the process to make the film from the fixation step much more durable. This can be done by light, heat or air. The paints for houses are cured by the reaction with oxygen in the air and they change from liquid to rigid dry film with high durability. Another example of curing is putting the coating material which is thermoset plastic in the oven.

The process of film formation for some coating material does not have to consist of all three steps. For example, in the case of lacquer, the steps of fixation and curing are combined into one step, that is, evaporating of the solvent during application.

1.2.3 Surface coating drying

Generally, the surface coating can be made dry by two procedures as follows;

1.2.3.1 Physical drying

The drying of this method can be achieved by the evaporation of solvents to become a film binding to the surface by weakly secondary bond. Therefore, the film can be dissolved in its solvents. The example includes lacquer and paint from chlorinated rubber.

1.2.3.2 Chemical drying

The film formed by this method binds to the surface by primary force from chemical reaction. Thus the film is stronger and higher resistance to solvents. This method can be operated in two ways:

1.2.3.2.1 By oxidation

The type of coating adsorb oxygen from the air. The oxidation reaction occurs and make the size of the particles bigger and combine to become dry and strong film. The example is oil paint from alkyd resin. This drying process can be accelerated by adding drier.

1.2.3.2.2 By chemical reaction

The reactants of this type of coating are put in separated containers and then are mixed with the ratio according to the manufacturer's recommendation. The strong and dry film results from the chemical reaction. If the reaction occurs at ambient temperature, the coating is called "cold curing coating". On the other hand, if the temperature is high, it is named "stoving or baking coating".

1.2.4 Solubility of polymers or resins

The dissolving process of polymer in normal solvents is different from that of smaller molecules. The obvious difference is that polymer dissolve a lot more slowly. Furthermore, the solvents are limited.

The dissolving process of polymer is vary slow and consists of two steps as follows:

First step when polymer solvents are mixed, the molecule of solvent more or diffuse slowly to polymer molecules slowly and make them expand to become swelling from the adsorption.

Second step: The swelling polymer will expand more to the point that the quantity of solvent is so high that the polymer chains can slip through each other and become fluid. This is stated to be complete solubility.

Highly crystalline polymers or cross-linked polymers do not perform the second step, therefore they do not dissolve but the only swell.

A polymer can be dissolved in solvents whose solubility parameters are similar to those of each polymer.

To predict the solubility of polymers to be to the real situation, the ability to form hydrogen bonding of solvents should be considered. This idea is originated by Burrell who classified solvents into three groups:

First group: poorly hydrogen bonded, δ_p , include aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated hydrocarbons and nitroparaffins.

Second group: moderately hydrogen bonded, δ_m , include esters, ethers and ketones.

Third group: strongly hydrogen bonded, δ_s , include alcohols, amines and acids.

The way solubility parameters can be used to easily predict the solubility is that polymer-solubility parameters of appropriate solvents should in the same rang as those of polymers.

Table 1.1 Solubility parameters of the solvents

<i>Aliphatic hydrocarbons</i>	δ_p
n-Hexane	7.3
n-Heptane	7.4
n-Octane	7.6
White spirit, 15% aromatic	7.5
White spirit, odorless	6.9
VM & P naphtha	7.6
Turpentine	8.1
Cyclohexane	8.2
<i>Aromatic hydrocarbons</i>	δ_p
Benzene	9.2
Toluene	8.9
Xylene	8.8
Tetrahydronaphthalene	9.5
<i>Chlorinated hydrocarbons</i>	δ_p
Methylene Chloride	9.7
Chloroform	9.3
Carbontetrachloride	8.6
Trichloroethylene	9.3
Chlorobenzene	9.5

Table 1.1 (Continued)

<i>Nitroparaffins</i>	δ_p	
Nitromethane	12.7	Table 1.1 (Continued)
Nitroethane	11.1	
Nitropropane	10.1	
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<i>Ethers</i>	δ_m	
<i>Ketones</i>	δ_m	
Dimethyl ether	9.8	
Cyclohexanone	9.9	
Diethyl ether	7.4	
Diethylene ether	8.9	
<i>Ethylene glycol monoalkyl ethers</i>	δ_m	
Ethylene glycol monomethyl ether	10.8	
<i>Esters</i>	δ_m	
Ethylene glycol monoethyl ether	9.9	
Methyl acetate	8.9	(Adapted from: Sorawaree, O., 1996, <i>Surface</i> <i>coatings (color,</i> <i>varnish and</i> <i>lacquer)</i> , 2 nd ed, B a n g k o k : Chulalongkorn University, p. 117)
Ethylene glycol monobutyl ether	8.9	
Ethyl acetate	9.1	
Propyl acetate	8.8	
<i>Alcohols</i>	δ_s	
n-Butyl acetate	8.5	
Methanol	14.5	
iso-Butyl acetate	8.3	
Ethanol	12.7	
n-Amyl acetate	8.5	
n-Propanol	11.9	
Methyl butyrate	8.9	
sec-Propanol	8.0	
Butyl butyrate	8.4	
n-Butanol	11.4	
di-Butyl phthalate	9.4	
sec-Butanol	10.8	
Ethylene carbonate	14.7	
tert-Butanol	10.6	
n-Octanol	10.3	
2-Ethylhexanol	9.5	
Acetone	10.0	
Ethylene glycol	14.2	
Methyl ethyl ketone	9.3	
Glycerol	16.5	
Diethyl ketone	8.8	
Methyl isobutyl ketone	8.4	I m p o r t a n t
<i>Water</i>	23.4	
Diacetone alcohol	9.2	

properties of solvents for surface coating industry includes solvency, volatility, spontaneous ignition temperature, flash point, chemical stability, color, odor, corrosive properties and cost (Sorawaree, 1996).

1.2.5 Solvent power or solvency

The dissolution of a polymer or a resin in a liquid is governed by the magnitude of the intermolecular forces between the molecules of the liquid and the molecules of the polymer resin. They are the same forces that govern the miscibility of liquids and the attraction between colloidal particles suspended in a liquid. Intermolecular forces have important influences on many factors for the appropriateness of paints. Therefore, they are worth considering here. There are three kinds of intermolecular force:

1.2.5.1 Dispersion or London forces arise as a result of molecular perturbation temporality but finite dipolar effect leads to an attraction between the molecules. In the case of hydrocarbons, this is the only molecular attraction.

1.2.5.2 Polar forces originate from the interaction between permanent dipoles or between dipoles and induced dipoles.

1.2.5.3 Hydrogen bonds when a hydrogen atom is attached to an electronegative atom such as oxygen or nitrogen, there is a shift in electron density from the hydrogen to the electronegative atom. Thus, the hydrogen atom acquires a small net positive charge and the electronegative atom becomes slightly negatively charged. The hydrogen can then interact with another electronegative atom within a second molecule to form a so-called hydrogen bond. These forces are responsible for such fundamental properties as the latent heat of vaporization, boiling point, surface tension, miscibility of course solvency (Lambourne and Strivens, 1999).

1.2.6 Volatility

Evaporation rate of various solvents for surface coating is of highly importance because fast evaporation rate results in fast film drying. However, incomplete film such as orange peeling or blushing can occur. On the other hand, the complete is obtained film if an evaporation rate is slow but the drying time can be too long (Sorawaree, 1996).

To get a suitable solvent mixture for surface coating, the rate of evaporation of the solvent in the process of application and must be considered curing. For example, thinners for motor refinishing can be formulated to have rapid or slow evaporation, up to the ambient conditions. Also, the rate of solvent loss from a thin film governs the speed of coating. The evaporation rate is important in selecting solvents. Finally, the evaporation causes increased viscosity. The flow is controlled by the solvent with lowest evaporation rate.

Evaporation essentially takes place in two stages. In the first step, the solvent loss is dependent on the vapor pressure of the solvent and is not markedly affected by the presence of dissolved polymer. In the second step, the polymer film is formed, the solvent is retained within the film and is subsequently lost by a slow diffusion-controlled process in this latter stage, as much as 20% of the solvent is retained in the film (Lambourne and Strivens, 1999).

1.2.7 Color and odor

The solvent for surface coatings must be colorless and odorless. The presence of color in the solvent can be due to contamination or decomposition during storage (Sorawaree, 1996).

1.3 Review of Literatures

There have been many researches concerning the determination of evaporation rate of solvent blends, surface coating material and solubility of a polymer. This interest is due to the importance of surface coating industry and the effect on environment. The researchers studying the determination of evaporation rate of solvent blends, surface coating material and solubility of a polymer are as follows:

Takahashi *et al.* studied resin composition for coating and coating composition for curing. The inventors provides polyol-containing resin compositions for coatings which can give cured coating films with high hardness and at the same time high solid compositions to meet the recent resources saving or environmental protection requirements, and curable coating compositions having high reactivity at curing, give the coating film with good appearance and the coatings with prolonged pot life. The invention is directed to a resin composition for coatings including a polyol (A1) or (A2), a polyether polyol (B) and a solvent (C), wherein the polyol (A1) consists of a hydroxyl-containing polymerizable unsaturated monomer and a ring structure-containing polymerizable unsaturated monomer as essential components and the polyol (A2) consists of a hydroxyl-containing polymerizable unsaturated monomer and a linear branched structure-containing polymerizable unsaturated monomer as essential components (Takahashi *et al.*, 2004).

Elhard and Heggs assigned color-forming composition including (i) a solvent absorbing material such as a polymer; (ii) a color-former or chelating agent compounded with the solvent absorbing material; (iii) a source of metal ions, whereby the metal ions complexed with the color former as the solvent absorbing material absorbs the solvent, resulting in a detectable

color change of the solvent absorbing material. These color-forming composition are supplied by both reversible and irreversible versions (Elhard and Heggs, 2004).

Glavchev *et al.* investigated rate of evaporation of mixed solvents with the formation of thin films for membranes base on cellulose triacetate. The evaporation rate of mixed solvents were determined by both gravimetry and gas chromatography (GC). Whilst gravimetry enables determination of the total rate of solvent mixture evaporation, GC gives the possibility of evaluating the individual rate of evaporation for each solvent (e.g. acetone and dioxane) used to generate a membrane (Glavchev *et al.*, 2003).

Segarceanu and Leca studied method to calculate Hensen solubility parameter, δ , comprising three parameters (dispersion, δ_d , polar, δ_p , and hydrogen bond, δ_h) as well as the radius of interaction sphere for a given polymer is presented, starting from the idea of the solvents which can dissolve a polymer. This paper concluded that good and limiting solvents of a polymer can be represented into the three-dimensional space of coordinate δ_d , δ_p , δ_h as system of material points with different weights (Figure 1.1), and the radius of interaction sphere the distance from this center to the farthest point of material points system mentioned.

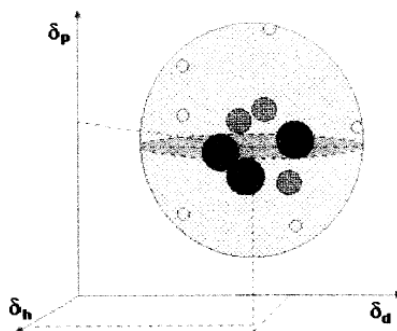


Figure 1.1 Scheme of interaction sphere of the studied resin.

It is obvious that the closer mass centre is with to solvents with higher weights, the better they can dissolve, compared those with smaller weights which are not good solvents for the polymer (Segarceanu and Leca, 1997).

Castells and Casella developed gas chromatography method that enables the determination of evaporation rate is to be able to measure the rate of individual components leave the mixture. The composition and temperature of the remaining liquid at any moment during the experiment were determined. The method offers definite advantages over the classical gravimetric methods (Castells and Casella, 1987).

Castells and Casella described a method is to be able to measure solvent evaporation rates under controlled condition. Vapors generated within a thermostated glass cell are swept by nitrogen current and periodically injected into a chromatographic column and detector by means of an automatic sampling valve. Solvent with evaporation rate is equal to or lower than that of cyclohexane. And the cooling effect is therefore quite small for solvents that evaporate under steady-state conditions, and the measured rate of evaporation can be referred to the cell temperature. The method offers a definite advantage over classical gravimetric techniques (Castells and Casella, 1987).

Van Dyk *et al.* studied three-component solubility parameters (nonpolar solubility parameter, δ_n , polar solubility parameter, δ_p , hydrogen bond solubility parameter, δ_h) is useful in predicting the solubility/nonsolubility of a polymers. The use of three-component solubility parameters is demonstrated in predicting both degree of solvency and solubility/nonsolubility. Predictability is significantly worse if the total solubility parameter is substituted for three-

component parameters. Predictability is significantly improved if the effect of solvent molar volume, V_m , on solubility is included. These conclusions are based on data for the solubility of three methacrylate polymers [poly(methyl methacrylate), poly(ethyl methacrylate), and poly(butyl methacrylate)] in 34 potential solvents (Van Dyk *et al.*, 1985).

Garner studied coating composition thinner for decreasing pollution resulting from the application of a coating composition. The method for decreasing the air pollution resulting from the application of paint by applying an organic solvent based paint and a water miscible organic solvent based thinner to a substrate thereby forming a gaseous effluent consisted of a mixture of air, gaseous organic solvent, gaseous thinner and passing the gaseous effluent into a gas absorbing means consisted of a non-reactive liquid solvent are described (Garner, 1982).

It is suggested from the previous studies that a solvent or solvent blend need to give the optimum results in any application. Various techniques have been developed to help establish optimum blends with the required solvency which is known as “solubility parameter systems”. Furthermore, factors influencing choices of solvent for any specific products includes solvency, evaporation rate, odor, toxicity, and the effect of air pollution. Finally, the evaporation rate can be determined by both gravimetry and gas chromatography (GC). However, GC method offers definite advantages over classical gravimetric methods because of being able to directly measure evaporation rate for each solvent.

1.4 Objective

To investigate the suitable solvent mixtures to dissolve the paints with low rate of evaporation.

1.5 Benefits

1.5.1 To get appropriate solvents for paint in plastic printing industry.

1.5.2 To reduce the problems of fast evaporating solvents which are costly.

1.5.3 Healthy and safe workplace environment of employees for who have risk of getting volatile solvents routinely.