

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Solder mask [1,2]

Solder masks provide a coating material used to mask or to protect selected and specific areas of a printed circuit board (PCB) from the action of an etching, soldering, or plating. Moreover, a solder mask is a coating, which masks off printed circuit board surface and prevents those areas from accepting any solder during vapor phase or wave soldering processing. The prime function of a solder mask is to restrict the molten solder pick up or flow to those areas of the printed circuit board, holes, pads and conductor lines.

##### 2.1.1 Classification of solder mask

The solder masks available are broadly divided into two categories, i.e. permanent solder mask and temporary solder mask. Two types of solder mask are screen printed onto a printed circuit board. Once printed, using either thermal or UV light cures the solder mask. After the mask is cured, it acts as a solder resist, selectively protecting the circuit during component soldering.

## **A distinction is made between permanent and temporary solder mask**

### **1. Permanent solder mask [2]**

Permanent solder mask compositions, which consist of tri-or poly-functional monomers, are highly cross-linked. This cross-linking prevents permanent solder masks from being soluble in organic solvents or water. Permanent solder mask is not made to be removed after curing. It becomes an integral part of PCB, which continually protects PCB from environment such as corrosive, heat, humidity and abrasion etc. throughout the life of the circuit board.

### **2. Temporary solder mask**

Temporary solder mask compositions do not contain tri-or poly-functional monomers. It is cured under a linear polymerization reaction. After curing, temporary solder mask can be removed from the board by organic solvents, water or even to be peeled off. Temporary solder mask is applied to a selected or limited area of a printed circuit board to protect certain holes or features such as connector fingers from accepting solder.

#### **2.1.2 The usually formula and composition of temporary solder mask**

The general temporary solder mask composition may comprise the following ingredients in the percentages indicated in table 2.1

**Table 2.1** General composition of temporary solder mask

Ingredient	Effective % by weight
Reactive diluent monomer	50-90
Thickener	1-15
Anti-oxidant	0.01-2
Initiator	1-10

The reactive dilute monomer of the above composition may be a substituted vinyl monomer, including allyl methacrylate, n-alkyl methacrylate (C<sub>2</sub>-C<sub>18</sub>), 2-ethoxyethyl acrylate, isodecyl methacrylate, lauryl methacrylate, 2-phenoxyethyl acrylate, benzyl acrylate, isobornyl methacrylate and isobornyl acrylate etc.

The thickeners in the above composition include silicon dioxide, carboxymethyl cellulose, carboxyethyl cellulose, xanthum gum, acacia gum and attapulgate clay etc.

The anti-oxidant of the above composition may include naphthoquinone, benzoquinone, alkyl or aryl-substituted naphthoquinones and alkyl or aryl-substituted benzoquinones etc.

The initiator is a free radical source I polymerization of the composition such as benzophenones, thioxanthenes, 2,2'-dimethoxy-2-phenylacetophenone, benzoyl peroxide, dicumyl peroxide and azobisisobutyronitrile etc.

Moreover, the above composition may be filled with releasing agent, plasticizer or oligomer to modify the properties of solder mask; such as easy and residue-free peelability, very high elasticity and tear resistance or very high temperature stability etc.

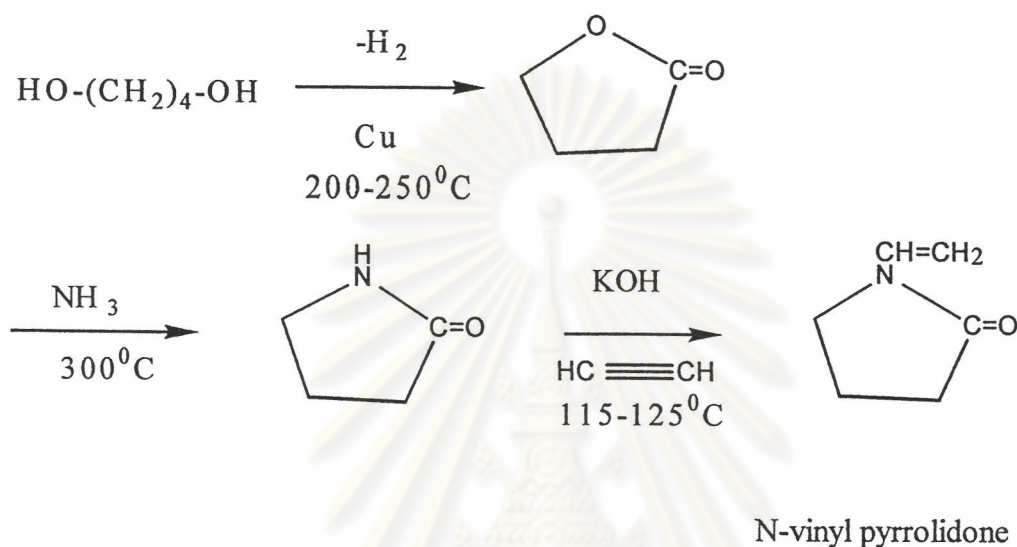
## 2.2 Reactive diluent monomer [3]

Most current coatings use acrylated reactants because acrylate cure more rapidly at room temperature and they are also less prone to oxygen inhibition. In general, the acrylate monomers range from mono- to hexafunctional, most commonly mixtures of mono-, di-, and trifunctional acrylates. The monomers are also called “reactive diluents”. Many multifunction acrylate monomers have been used; examples are trimethylolpropane triacrylate, pentaerythritol triacrylate, 1,6-hexanediol diacrylate, and tripropyleneglycol diacrylate. Care must be used in handling them because many are skin irritants and some are sensitizers. A range of monofunctional acrylates has been used but they may be too volatile. 2-Hydroxyethyl acrylate has sufficiently low volatility and high reactivity but the toxic hazard is too great in many applications. N-Vinyl pyrrolidone is an example of a nonacrylate monomer that copolymerizes with acrylates at speeds comparable to acrylate polymerization; N-vinyl pyrrolidone is particularly useful because the amide structure promotes adhesion to metal and reduces oxygen inhibition.

### 2.2.1 N-vinyl pyrrolidone [4,5]

N-vinyl pyrrolidone (NVP), IUPAC called N-vinyl-2-pyrrolidinone was developed in Germany at the beginning of World War II. The principal use of N-vinyl pyrrolidone is as a monomer for the preparation of Poly (N-vinyl pyrrolidone)(PVP) homopolymer and various copolymers. The poly (N-vinyl pyrrolidone) is used in cosmetic formulations, especially hair lacquers because poly (N-vinyl pyrrolidone) is the preferred film-former on account of good adhesion to hair, which is removed by

washing. Moreover, this polymer is used as a binder in pharmaceutical tablets and in the textile industry. The N-vinyl pyrrolidone is prepared from 1,4- butanediol as in the following diagram 2.1.



**Diagram 2.1** Show preparation of N-vinyl pyrrolidone [6]

### 2.2.1.1 Properties of N-vinyl pyrrolidone

N-vinyl pyrrolidone are readily polymerized by both cationic and free radical catalysis and yield stable polymers with a variety of molecular weights. They also readily copolymerize under free-radical condition with monomers of negative  $r$  value, eg. vinyl acetate,  $r = -0.22$  and with positive value, eg. methylmethacrylate,  $r = 0.40$ .

The physical properties of N-vinyl pyrrolidone are shown in table 2.2.

**Table 2.2** Properties of N-vinyl pyrrolidone [5]

Properties	Value
Freezing point, °C	13.5
Boiling point, °C <sub>kPa</sub>	46 <sub>0.1333</sub>
	147 <sub>13.3</sub>
Density, g/cm <sup>3</sup> at 25 °C	1.04
Refractive index	1.511
Viscosity at 25°C, mPa-s	2.07
Flash point, open cup, °C	98.4
Firepoint, °C	100.5

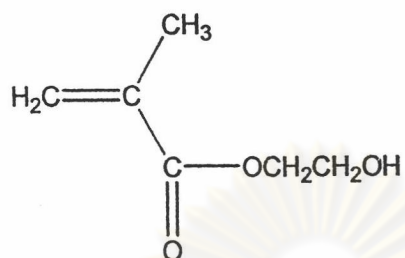
The glass-transition-temperature of poly (N-vinyl pyrrolidone) is 175 °C. The melt viscosity is too high for typical thermoplastic forming operation. Film of Poly (N-vinyl pyrrolidone) are clear, transparent, glossy and hard.[6]

### 2.2.2 Hydroxypropyl methacrylate [7]

Vinyl polymers, thermoplastic methacrylics are generally considered inert unless certain functional groups are purposely added to the polymer chain for eventual crosslinking. They exhibit good resistance to hydrolysis and ultraviolet degradation. Other important properties usually associated with thermoplastic methacrylics are:

- 1) Transparent water-clear film appearance
- 2) Low pigment reactivity

- 3) Compatibility with other film formers
- 4) Chemical and water resistance
- 5) Resistance to chemical fumes



**Figure 2.1** The structure of hydroxypropyl methacrylate

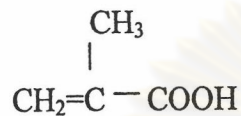
**Table 2.3** The general physical properties of 2-hydroxypropyl methacrylate

Properties	Value
Molecular weight	144.17
Boiling point, °C	205-209
Density, g/cm <sup>3</sup> at 25 °C	1.066
Glass transition (T <sub>g</sub> ), °C	73

## 2.3 Compounding Ingredients

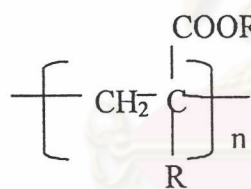
### 2.3.1 Acrylic Polymers

The ranges of acrylic and methacrylic polymers are based upon monomers of acrylic acid  $\text{CH}_2=\text{CH}-\text{COOH}$  and methacrylic acid.



These are easily polymerized or copolymerised with other commoners because of their highly reactive double bonds and miscibility with oil-soluble and water-soluble monomers. Polymerization can be carried out by bulk, solution, suspension or emulsion techniques using a variety of catalysts.

The general formula for an acrylic homopolymer is



Where R represents H or  $\text{CH}_3$ ,  $\text{R}'$  represents H, alkyl, alkoxy, alkenyl or an aryl radical, and  $n$  = degree of polymerization [8]

Acrylic polymers for protective coatings were first produced as commercial products in the 1930s. The three principal forms of acrylic polymer used in surface coatings are:

- a) Thermoplastic dispersion, that is acrylic latex,
- b) Thermoplastic solution
- c) Thermosetting solution



Acrylic polymers are used for applying adhesives, coating, and inks. The use of acrylic polymers for both emulsion and solution coatings which consider to follow Table 2.4

**Table 2.4** Glass transition temperature versus application area [9]

Glass-transition ( $T_g$ ) °C	Suggested application area
80-100	High heat resistant coatings
50-65	Flour are coatings
35-50	General industrial coatings
10-40	Decorative paints
25-35	Binders for inks
-60-25	Adhesives

### Properties and using

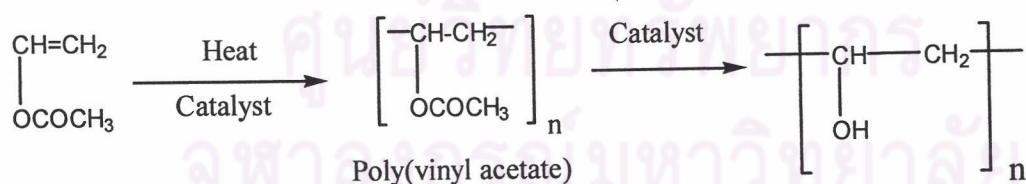
Acrylic polymer is generally considered inert unless the functional groups are purposely added to the polymer chain of eventual cross-linking. They exhibit good resistance to hydrolysis and ultraviolet degradation, which accounts for their outstanding exterior durability. Other important properties usually associated with thermoplastic acrylics are:

- Transparent water-clear film formers
- Low pigment reactivity
- Compatibility with other film formers
- Chemical and water resistance
- Resistance to chemical fumes

### 2.3.2 Poly(vinyl Alcohol)

The Du Pont Company commercially introduced polyvinyl alcohol, first synthesized in Germany in 1925, in the United States in 1939. Chemically, polyvinyl alcohol can be classified broadly as a polyhydric alcohol with secondary hydroxyl groups on alternate carbon atoms. In producing polyvinyl alcohol resin a multistep process is used since vinyl alcohol monomer is a non-existent entity, rapidly rearranging itself to acetaldehyde. Thus, it is first necessary to produce polyvinyl acetate resin from vinyl acetate monomer, and follow with the alcoholysis of the polyvinyl acetate to polyvinyl alcohol.

These reactions are illustrated as follows:



Properties of polyvinyl alcohol, both completely and partially alcoholized polyvinyl alcohols have many characteristics in common which make the polymer valuable to a number of industries. This poly(vinyl alcohol) is used two types (PVA)

(GH-17) and PVA (GL-5)) in this research, which has physical properties in Table 2.5 and Table 2.6

**Table 2.5** Physical properties of poly(vinyl alcohol) (GL-05)

Properties	Value
Appearance	Colorless crystalline
Viscosity (4% aqueous solution)(25°C)	4-10 cps
pH (10% aqueous solution)	4-7
% Loss on drying	5.0 max
Hydrolysis (%mol)	87-89
Solubility	Water or Hot water

**Table 2.6** Physical properties of poly(vinyl alcohol) (GH-17)

Properties	Value
Appearance	Clear crystalline
Viscosity (4% aqueous solution)(25°C)	20-25 cps
pH (10% aqueous solution)	5-7
% Loss on drying	5.0 max
Hydrolysis (%mol)	87-89

Film formation, poly(vinyl alcohol) generally is dissolved in water prior to use, its film-forming abilities are of extreme importance in most applications. Polyvinyl alcohol films and coatings do not require a curing cycle, film formation occurring readily by simple evaporation of water from the solution. When compared with plastics, the tensile strength of polyvinyl alcohol is high and when compared with other water-soluble materials, it is very impressive. The tensile strength of polyvinyl alcohol varies with a number of factors including percent hydrolysis, which tensile strength values increase as the percent hydrolysis increase.

### 2.3.3 White pigments and extenders

Pigments may be added to a coating in order to cheapen and stiffen the product, or to color it. White pigments and extenders, as well as carbon blacks, have been described separately from other pigments, as special description of types and other properties is essential. The most effective white pigment available for coating work is rutile titanium dioxide. The anatase type may also be used.

**Table 2.7** White pigments and extenders

Description	Oil Absorption	Transparency Or Opacity	Soap Resistance	Alkali Resistance	Special Properties	Particle Size ( $\mu\text{m}$ )
Zinc dioxide	12	Semi-transparent	Good	Good	Not acid resistant	0.3-0.4
Titanium dioxide	20	Opaque	Good	Good	„	0.2-0.3
Calcium carbonate	30	Transparent	Good	Good	„	
Talc	40	Transparent	Good	Good	„	0.3-1.0

### Calcium carbonates

In this group of fillers are included the various whiting, chalks and limestone. All are very cheap and all give poor quality products with a marked tendency to discoloration.

### Zinc oxide

The general properties of Zinc oxide are clean white of medium opacity, strong UV absorber, neutralizes acidic oxidation products, and fine ground particle size. It is used as white extender in tin printing and many other ink systems. It improves flow and leveling.

### Titanium dioxide

Titanium dioxide is opaque white pigment. A property of Titanium dioxide is resistant to everything; very light fast and heat resistant. It is provided two major grades, i.e. Rutile (harder, bluer, more opaque than Anatase) and Anatase (less opaque, more stable except in tint, softer texture)[10]

It is used for cheaper water-based flexor inks, screen process inks and some gravure whites.

#### Formula and composition

TiO <sub>2</sub>	80-99.9 %
( Al, Si or Zn)O	0-20 %

**Table 2.8** Typical properties [11]

	<b>Anatase</b>	<b>Rutile</b>
Pigment Form	Brilliant white	Powders
Density (g/cm <sup>3</sup> )	3.8-4.1	3.9-4.2
Refractive index	2.55	2.76
Oil absorption (lb/100lb)	18.30	16.48
Particle size (μm)	0.3	0.2-0.3

The rutile has greater density, hardness, and higher refractive index than the anatase.

Although the rutile is more expensive to produce, however the rutile is generally preferred for the pigmentation of plastics and surface coatings which may be exposed to sunlight.

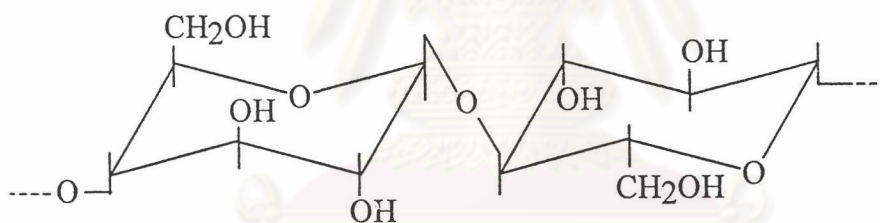
#### 2.3.4 Thickening agent

All of the substances to be considered in this section may be described loosely as *hydrocolloids*. They are soluble in water to give viscous solutions. Many of these substances occur naturally as the products of animal or plant metabolism, or are derivatives of such products. A few synthetic substances have become available in recent years.

Considered as a group, the substances under review here find their principal application in latex technology as modifiers of bulk flow behavior. They are often referred to vaguely as *thickeners*. The substances are also functioned as dispersion and emulsion stabilizers, and in this respect they are often referred to as *protective colloids*. While they are sometimes added to disperse systems in order to enhance the colloid stability, it is important to realize that it is not possible to separate the effects upon flow behavior from the effects upon stability

The examples of substances in this group are following:

**Cellulose Derivatives** Cellulose is a linear poly1,4- $\beta$ -D-anhydrogluco-pyranose (Structure III), of molecular weight between 200,000 and 800,000, depending upon its source.



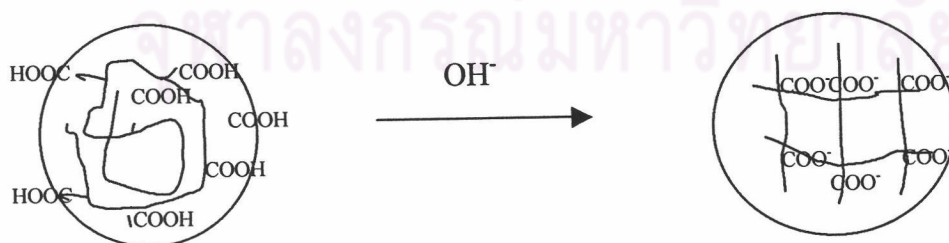
Each cellulose molecule may therefore contain between about 1,300 and 5,000 glucose units. [12]

**Carboxyalkyl ethers** The only important members of this group are the sodium salts of carboxymethyl cellulose. They are formed by reaction between the sodium salt of chloroacetic acid and sodium cellulose. While the free acids (which are moderately strong) are not very soluble in water, the sodium salts are. The latter do not precipitate from solution upon heating. Acids and heavy metal ions are not greatly affected, although the precise effects depend to some extent upon the chain length and upon the degree of substitution.

All the cellulose ethers are very stable and may be stored for long periods without change. They are somewhat hygroscopic in damp atmospheres. Their aqueous solutions are very much less prone to attack by microorganisms than are the solutions of gums, starches, proteins and alginates. However, it is wise to include a preservative if maintenance of viscosity is desired over long periods.

*Carboxyvinyl polymers or Carbopol* is crosslinked carboxyvinyl polymer, which suddenly disperse in water (polymer latex) to obtain low viscosity acidic dispersion. When it is filled with suitable base such as alkylol amines, long chain fatty amines or sodium hydroxide, potassium hydroxide that it will be gel and high viscosity.

The thickening of polymer latex systems is required for a wide variety of applications. Water-soluble polymer crosslinked carboxyvinyl polymers are effective latex thickeners. With any given water-soluble polymer, thickening of the latex is increased with increased molecular weight of the thickener, which indicates some support for the requirement of thickening the aqueous phase. This variability of thickening action is typical and may be attributed to the various latex compositions, particularly the nature of the emulsifier. The phenomenon is made even more complex with compounded latex formulations in which the thickener may also react with clay, pigment and fillers introduced into system.



**Figure 2.2** The arrangement of carbopol after fill hydroxide



## Xanthan gum

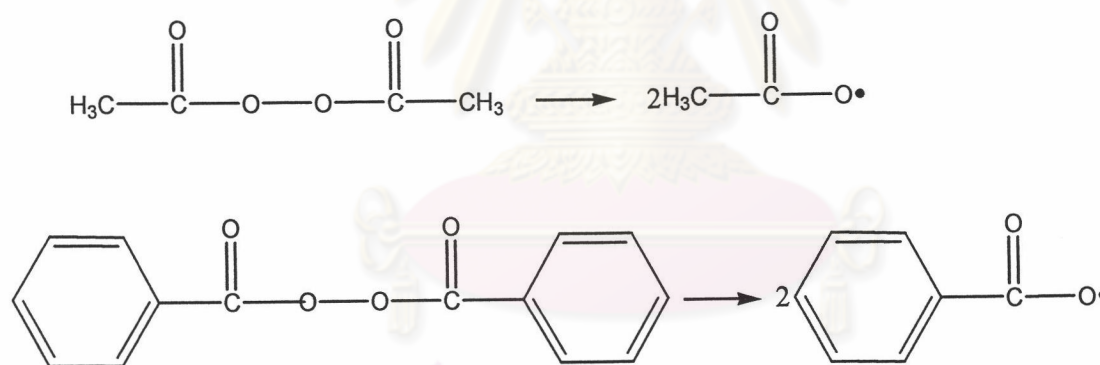
Xanthan gum is a water-soluble gum, which, in a purified state, is designated as cellulose gum. Many applications of cellulose gum follow the pattern set by naturally occurring vegetable gums. Xanthan gum is Thickening and stabilizing hydrocolloid (MW  $\approx$  2,500,000) giving aqueous solution of high viscosity and high yield value even at low concentrations not affected temperature. Pseudoplastic non-thixotropic behavior. Effective suspending and stabilizing agent for multiphase systems: aqueous suspensions, emulsions and foams.

**Table 2.9** General physical properties of Xanthan gum

Property	Value
Appearance	White to cream-colored fine powder
pH(1% aqueous solution)	5-7
% Loss on Drying	10 max
Viscosity(1%aqueous solution)(25°C)	4,000-6,000 cps
Particle size distribution	95% minimum through 175 $\mu$ m

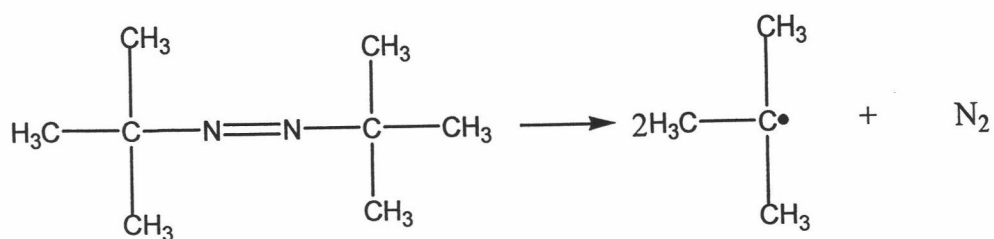
### 2.3.5 Thermal initiator

Polymerizations initiated in radical polymerization are often referred to as thermal initiated or thermal catalyzed polymerizations. The number of different types of compounds that can be used as thermal initiators is rather limited. One is usually limited to compounds with bond dissociation energies in the range 100-170 KJ/mole. Compounds with higher or lower dissociation energies will dissociate too slowly or too rapidly. Only a few classes of compounds including those with O-O, S-S, N-O bonds possess the desired range of dissociation energies. The examples of thermal initiator are peroxy compounds such as benzoyl peroxides, t-butyl peroxides, cumyl hydroperoxides etc. [13]



**Figure 2.3** The decomposition of acetyl peroxide and benzoyl peroxide

Moreover, the azo compound, 2,2'-azobisisobutyronitrile (AIBN), is the most important member of this class of initiators.



**Figure 2.4** The decomposition of 2,2'-azobisisobutyronitrile (AIBN)

**Table 2.10** Half-life of Initiators

Initiator	Half-Life at								
	50°C	60°C	70°C	85°C	100°C	115°C	130°C	145°C	155°C
Azobisisobutyronitrile	74hr		4.8hr		72hr				
Benzoyl peroxide			7.3hr	1.4hr	19.8hr				
Acetyl peroxide	158hr		8.1hr	1.1hr					
Lauryl peroxide	47.7hr		3.5hr	31min					
t-Butyl peracetate				88hr	12.5hr	1.9hr	18min		
Cumyl peroxide		12.8hr				13hr	1.7hr	16.8hr	
t-Butyl peroxide					218hr	34hr	6.4hr	1.38hr	
t-Butyl hydroperoxide					338hr				44.9hr

### 2.3.6 Inhibitors

The most useful class of inhibitors are molecules that react with chain radicals to yield radicals of low reactivity. Quinones such as benzoquinone and chloranil (2,3,5,6-tetrachlorobenzoquinone) are an important class of inhibitor. Two major types of products are obtained quinone and ether formed by reaction at the C and O atoms of a quinone, respectively. Attack of a propagating radical at oxygen, which can terminate by coupling and/or disproportionation with another propagating radical or add monomer. [14]

## 2.4 Literature Review

G.R.Unruh [15] studied a composition of an ultraviolet curable temporary solder mask which included

- Photoinitiator
- Antioxidant
- Reactive diluent monomer capable of polymerization,
- Thickener

Solder mask in this work does not use any solvent, therefore they have minimal health and environmental concern. Moreover, this solder mask could be removed from the surface to be protected by either dissolving this temporary solder mask in an aqueous non-alkaline solution, an organic solvent or peeling the mask off of the protected surface.

T. Matynia, R. Kutyla, K. Bukat and B. Prenkowska [16] studied the properties of solder masks which prepared from epoxyacrylic, epoxymethacrylic ester, and monomers such as 2-ethylhexyl acrylate, triethylene glycol dimethacrylate, and triethylene glycol phthalate dimethacrylate. This Solder mask is hardenable by ultraviolet radiation. They investigated suitable parameters characterizing the solder mask such as viscosity, adhesion to the surface, thermal resistance and the concentration of the UV polymerization initiator and filler.

In the case of masks based on epoxyacrylate oligomers in which the mixture of 2-ethylhexyl acrylate and triethylene glycol dimethacrylate used in crosslinking, the viscosity decrease from 290,000 to 60,000 Cp and good printability was obtained. The addition of 2-4 % of each photoinitiator does not affect mask printability but it improves the adhesion to the surface and resistance to soldering. The mask containing 3 % of the photoinitiator shows sufficient adhesion to copper.

K.F. Drain, R. Summers and L.A. Nativi [17] studied the composition and method for providing radiation curable temporary solder mask of electrical and electronic components compatible with a high-speed production operation. The composition is a radiation curable viscous liquid, including monomers such as acrylic monomers, unsaturated polyesters, thiol-ene formulations, and formulations base on other vinyl monomers such as N-vinyl pyrrolidone, vinyl acetate, styrene, etc. The cured composition of these monomers have sufficient cohesion strength to allow to be stripped off in a single piece. Vinyl stearate monomer or high levels of plasticizer or filler, such as a fumed silica, were used to reduce the adhesion of the cured composition to the substrate by suitable adhesion in the tensile shear mode between 5-55 psi. This level of adhesion is sufficient to prevent ingress the wave soldering or

vapor phase soldering i.e. immersion in molten solder at 525°F in approximately 10-30 seconds but low enough to allow easy dry stripping mechanically or by hand.

T. Maeda, Y. Sasagawa, Y. Ikeda and T. Hiraharu [18] studied water-based maskant composition comprising of 100 parts by weight (as solids) of a latex constituent consisting of (a) 5-60 parts by weight (as solids) of copolymer latex obtained by emulsion-polymerization of monomer mixture consisting of 30-70% by weight of an aliphatic conjugated diene compound, 20-70% by weight of an aromatic vinyl compound, 0-10% by weight of an ethylenically unsaturated carboxylic acid and 0-50% by weight of a vinyl compound copolymerizable therewith and (b) 94-50 parts by weight (as solids) of a natural rubber latex.

The filler included calcium carbonate, talc, clay, magnesium carbonate, magnesium hydroxide, etc. The amount of filler used is 10-150 parts by weight, per 100 parts by weight (as solids) of the latex constituent. The thickener includes carboxymethylcellulose, polyvinyl alcohol, and crosslinking type acrylic emulsion. The amount of the thickener used is 0.1-10 parts by weight, preferably 1-3 parts by weight per 100 parts by weight (as solids) of the latex constituent. Tensile strength and elongation of a film obtained from the composition are 50-150 kgf/cm<sup>2</sup> and 100-800%, respectively

M.A. Khan, K.M. Idriss, M.M. Zaman, and M.A. Hossain [19] studied ultraviolet curable leather surface coating material including urethane oligomer, reactive diluent such as N-vinyl pyrrolidone, butanediol diacrylate, tripropylene glycol diacrylate and trimethylolpropane triacrylate, photoinitiator (Irgacure 184). Their properties were characterized. The effect of codiluents of low glass transition temperatures like ethyl

hexyl acrylate and methoxyethyl acrylate on the properties of these films was studied. These formulations were then applied as thin coatings on the leather surface in order to study the improvement of the leather substrate, which increased tensile strength and elongation of the leather. The formulations comprised of 60 % oligomer, 5% photoinitiator, 17 % diluent's monomer and 18 %w/w codiluent monomer.

Y. Chin Lai [20] studied the effect of crosslinkers in photocopolymerization of N-vinylpyrrolidone and hydroxyethyl methacrylate. It was found that crosslinkers with a vinyl carbonate group can copolymerize with N-vinyl pyrrolidone better than those containing an allyl group, which in turn are better than those containing a methacrylate group. A crosslinker with a vinyl carbonate and a methacrylate group can copolymerize with N-vinyl pyrrolidone and hydroxypropyl methacrylate better in terms of giving hydrogels with the highest water content.



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