

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Solder Mask [1,4]

Solder masks or solder resists are coating materials used to mask or protect selected areas of a PCB from the action of an etching, soldering or plating. The prime function of a solder mask is to restrict the molten solder pickup or flow to those areas of the PCB, holes, pads and conductor lines that are not covered by the solder mask.

A somewhat more useful working definition for a solder mask is as follows: a coating which masks off a PCB surface and prevents those areas from accepting any solder during vapor phase or wave soldering processes.

2.1.1 Classification of Solder Mask

The available solder masks are broadly divided into two categories, i.e., permanent solder masks and temporary solder masks. The breakdown of the solder mask types is shown in Figure 2.1.

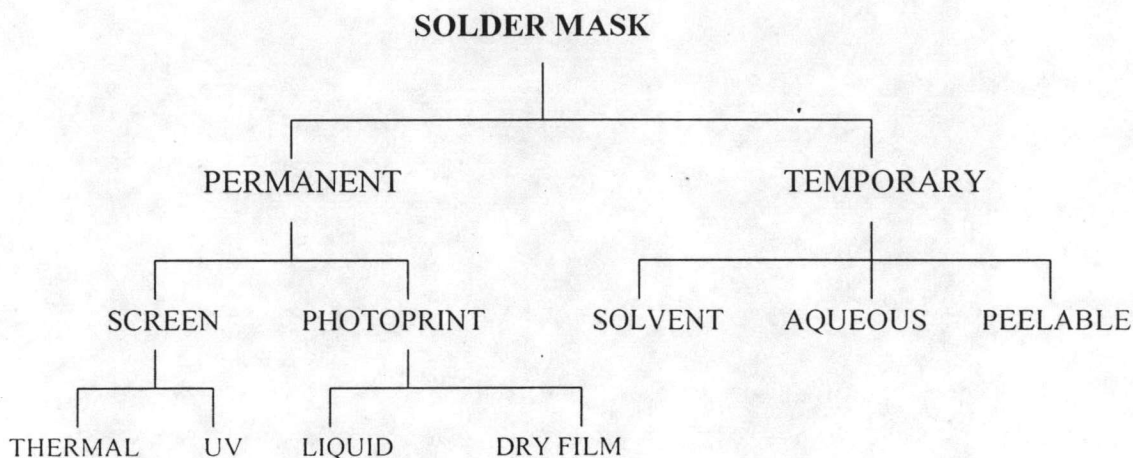


Figure 2.1 Solder mask selection tree.

The permanent solder mask materials are classified by the means used to image the solder mask, i.e., screen printing or photoprint. In addition, the screen-printed masks are further classified by the curing technique, i.e., thermal or ultraviolet (UV) curing. The photoprint solder masks are distinguished from each other by whether they are in the form of liquid or dry film. The temporary mask materials are classified by chemistry or means of development.

i) Permanent Solder Mask [4]

Permanent solder mask are not removed and thus become an integral part of PCB. Their compositions, which consist of tri- or poly-functional monomers, are highly cross-linked upon curing of via ultraviolet light or electron beam. This cross-linking prevents permanent solder masks from being soluble in organic solvents or water.

ii) Temporary Solder Mask

Temporary solder masks do not contain tri- or poly-functional monomers and therefore do not cross-link upon curing. Rather, temporary solder masks, upon curing, undergo a linear polymerization reaction, thus allowing the temporary solder mask to be soluble in organic solvents, water or even to be peeled off from a circuit board. The solubility of temporary and permanent solder masks is crucial to the utilization of these masks in the electronic industry. Temporary solder masks are applied to a selected or limited area of a PCB to protect certain holes or features such as connector fingers from accepting solder. The temporary solder mask keeps solder out of the selected holes and thus allows for certain process or temperature sensitive components to be added manually at a later time.

2.2 Natural Rubber [5,6]

Natural latex concentrates have been commercially available since about 1930 and subsequently have been thoroughly exploited for the manufacture of a great variety of products. The several methods of concentrating the latex, by heating, by creaming, centrifugally or chemically and later by electrodecantation, encouraged these developments because less water was transported and because higher solid contents increased still further its advantage over solutions of rubber in organic solvents for some manufacturing operations.

2.2.1 Properties of Raw Natural Rubber [7]

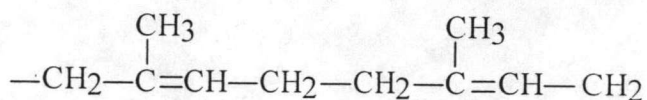
Natural rubber latex consists of particles of rubber hydrocarbon and non-rubbers suspended in an aqueous serum phase. The average dry-rubber content of latex may range between 30% and 45%. A typical composition of fresh latex is shown in Table 2.1. The rubber hydrocarbon in freshly tapped latex is almost completely soluble (more than 95%) in common solvents such as toluene and tetrahydrofuran. It has a chemical structure of almost 100% cis-1,4-polyisoprene units.

Table 2.1 Typical composition of Fresh Latex and Dry Rubber[7].

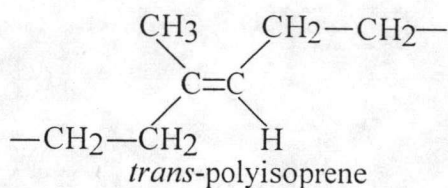
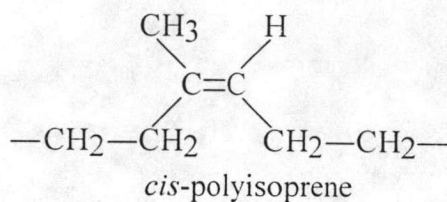
Composition	Latex, %	Dry rubber, %
Rubber hydrocarbon	36	93.7
Protein	1.4	2.2
Carbohydrates	1.6	0.4
Neutral lipids	1.0	2.4
Glycolipids + Phospholipids	0.6	1.0
Inorganic constituents	0.5	0.2
Others	0.4	0.1
Water	58.5	-

2.2.2 Chemical Formula of Natural Rubber[8]

Natural rubber is a polymer of isoprene, in which essentially all the isoprene units are linked together at carbon atom 1 and 4 in a head-to-tail arrangement, and in which all or nearly all the repeating units possess the "cis" configuration.



Head-to-tail arrangement



Natural rubber is the *cis*-polymer which the unit cell structure of the crystalline stretched rubber molecule is shown in Figure 2.2.

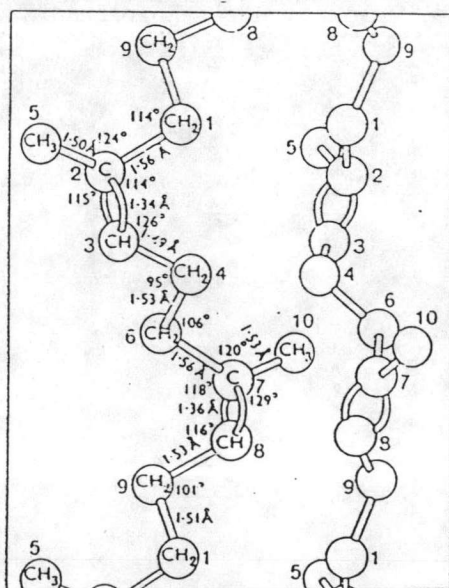
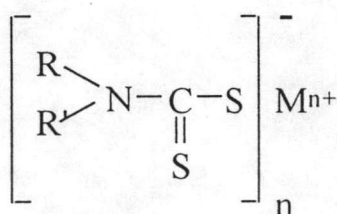


Figure 2.2 Unit cell structure of the natural rubber molecule[8].

metallic and amine dialkyl dithiocarbamates. The salts of the dialkyl dithiocarbamic acids have the generic structure as shown below (II). In theory the two alkyl groups of any one molecule may be different, but in practice they are usually identical.

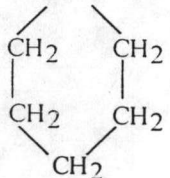
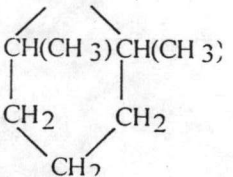
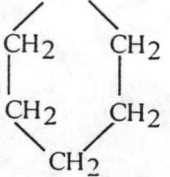
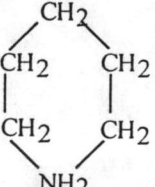


II

The cation may be either a metal ion or a derivative of ammonium ion. An important distinction between the amine and alkali metal salts on the one hand, and those of polyvalent metallic cations on the other, is that the former are soluble in water (although sparingly so in some cases), whereas the latter are not. Note that the heavy metal derivatives are most conveniently formulated as salts.

Some of the more common dialkyl dithiocarbamates, which find application in latex technology are listed in Table 2.2. Although a considerable range is available, it is probably true to say that zinc diethyl dithiocarbamate is by far the most widely used of the dithiocarbamates, indeed of all latex accelerators.

Table 2.2 Some typical dialkyl dithiocarbamates.

Full name	Common abbreviation	M	n	R, R'	I or S*
Zinc diethyl dithiocarbamate	ZDC	Zn	2	C ₂ H ₅ , C ₂ H ₅	I
Zinc dimethyl dithiocarbamate	ZMDC	Zn	2	CH ₃ , CH ₃	I
Zinc dibutyl dithiocarbamate	ZBDC	Zn	2	n-C ₄ H ₉ , n-C ₄ H ₉	I
Zinc dipentamethylene dithiocarbamate	ZPDC	Zn	2		I
Zinc lupetidine dithiocarbamate	ZL(DC)	Zn	2		I
Sodium diethyl dithiocarbamate	SDC	Na	2	C ₂ H ₅ , C ₂ H ₅	S
Sodium pentamethylene dithiocarbamate	SPDC	Na	1		S
Piperidinium pentamethylene dithiocarbamate	PPDC		1		S

*I: insoluble in water

S: soluble in water

An important variable at the choice of the compound formulator is whether to specify a soluble or an insoluble dithiocarbamate. The water-soluble dithiocarbamates are easier to add to latex than are the insoluble ones, but they are also less active as accelerators.

2.3.3 Viscosity modifiers and protective colloids [9,10]

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*. These substances also function 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 effects upon flow behavior from effects upon stability.

The examples of substances in this group are following:

i) Casein For the latex technologist, the most important protein is casein. It is a phosphoprotein which is obtained from caseinogen, the raw protein of milk. The most useful product is obtained from milk whey by acid precipitation, either by the addition of mineral acid (in which case the product is known as *acid casein*), or by allowing lactic acid to develop spontaneously.

Acid casein has a molecular weight of the order of 40,000. There is some evidence, which suggests that it is a single molecular species. As usually encountered, it is a very pale, buff-colored powder which contains some 10% of moisture. It has a characteristic odor. It is very sparingly soluble in water, but is readily soluble in acid and alkalis-its solubility as a function of pH is indicated in Figure 2.3.

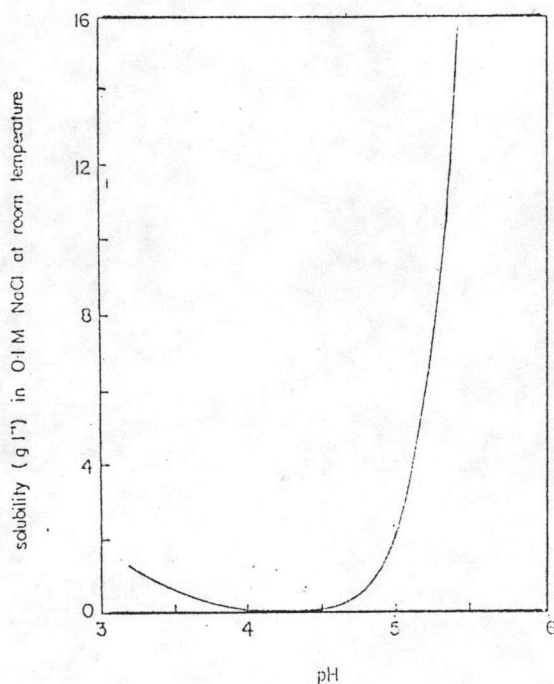
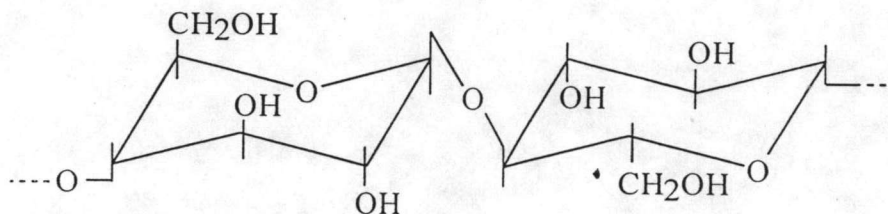


Figure 2.3 Effect of pH upon solubility of casein.

The isoelectric point of acid casein is in the region of pH 4.6. It finds application in latex technology primarily as a protective colloid, dispersion stabilizer and thickener. If required to store casein solutions for any length of time, it is important to add preservatives such as sodium pentachlorophenate. Solutions of casein are mildly surface-active.

ii) **Cellulose Derivatives** Cellulose is a linear poly1,4- β -D-anhydroglucopyranose (Structure III), of molecular weight between 200,000 and 800,000, depending upon its source.



III

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

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. 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.

The effect of concentrations upon the viscosity of aqueous solutions of various cellulose ethers is illustrated in Figure 2.4. A curve for sodium alginate is included for comparison. It should be noted that solutions of sodium carboxymethyl cellulose

are often markedly thixotropic in behavior, and that good use may sometimes be made of this effect.

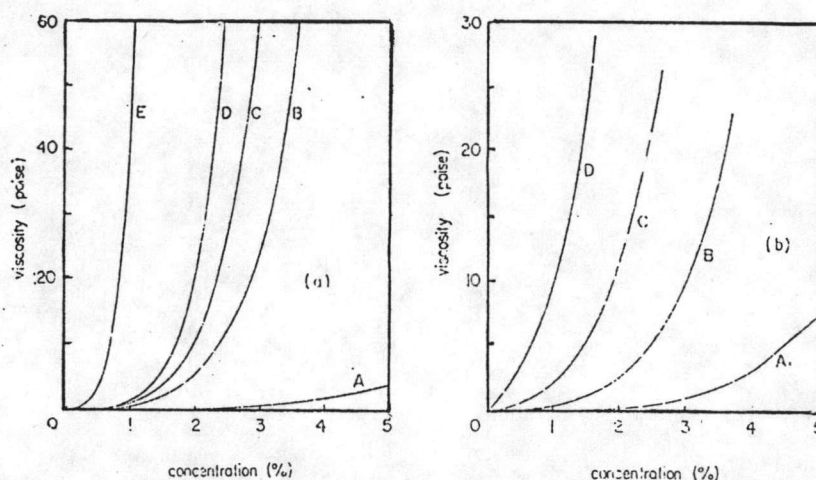


Figure 2.4 Viscosity-concentration relationships for aqueous solutions of several cellulose ethers.

Key: (a) A, B, C, D-various grades of methyl cellulose at 20°C

E- sodium alginate in 0.1M NaCl at 25°C (included for comparison purposes)

(b) A-“low viscosity” sodium carboxymethyl cellulose

B-“medium viscosity” sodium carboxymethyl cellulose

C-“high viscosity” sodium carboxymethyl cellulose

D-“extra viscosity” sodium carboxymethyl cellulose

all at 20°C, 68 sec⁻¹ shear rate

2.3.4 Surface-Active Agents [9,10]

Surface-active agents are substances which bring about marked modifications in the surface properties of aqueous media, even though they are present only in very small amounts (of the order of 1% or less).

A great number of surface-active agent substances currently available may be usefully classified in two distinct ways. In the first method classification is by function, and the classes are *wetting agents*, *dispersing agents*, *dispersion stabilizers*, *emulsifiers*, *foam promoters*, *foam stabilizers*, etc. It is a disadvantage of this method of classification that the groups are not mutually exclusive. There being a considerable degree of overlap. This seems to be inevitable when any attempt is made to classify by function. Thus a soap such as potassium oleate could be placed in any one of the above groups, since it is capable of functioning effectively in all of these capacities.

The second method classification is by chemical nature, and divides surface-active agents into *anionic*, *cationic*, *amphoteric* and *non-ionogenic* types, according to the active entity of the substance which is an anion, a cation, an amphoteric ion or a neutral molecule.

Anionic surface-active agents This is the most important group of surface-active substances from the point of view of latex technology. Of the large number of substances which come into this group, those organic compounds of interest to the latex technologist fall under three headings: carboxylates, sulfonates and sulfates.

i) *Carboxylates* For this class, the surface-active anion is of the type $R-CO_2^-$, where R may be a long-chain aliphatic hydrocarbon radical (as in the stearates and oleates) or a complex hydrocarbon ring system (as in the rosin acid soaps).

ii) *Sulfonates* For this second principal sub-group of anionic surface-active compounds, the active ion is of the form $R-SO_3^-$. As a sub-group, the sulfonates are very much less sensitive to acids and heavy metal ions than are the carboxylates.

iii) *Sulfates* The surface-active ion for this sub-group is of the type $R-SO_4^-$ (or $RO-SO_3^-$). In general the substances of this class are all strongly surface-active,

and find application as wetting agents, dispersing agents and dispersion stabilizers. They are more soluble in water than are the corresponding sulfonates.

Cationic surface-active agents The members of this group have the characteristic that their surface-activity is attributable to a cation. The most of cationic surface-active agents which are of interest to the latex technologist, the cation is derived from the ammonium ion by replacement of one or more of its hydrogen atoms with organic moieties.

Amphoteric surface-active agents In this group of substances, the surface-active component of the molecule may be a dipolar ion (zwitterion) or it may be either an anion or a cation according to the prevailing conditions of pH. The most important members of this group are the water-soluble proteins, but these are only mildly surface-active and are in fact used mainly as protective colloids and viscosity modifiers.

Non-ionogenic surface-active agents The types of interest to the latex technologist are usually the condensation products of ethylene oxide with fatty acids, fatty alcohols or phenols.

A most useful product is marketed under the trade name of Vulcastab LW. It is said to be of the polyethylene oxide condensate type, but the precise details of its composition have not been disclosed.

Polyethylene oxide condensates are very useful as emulsifying agents and as stabilizers. In this latter respect they are of value as stabilizers for both latices and for dispersions of insoluble powders. They are superior to natural products, such as

casein, in that they are less variable in character and their aqueous solutions are subject to putrefaction. They have the unusual property of being less soluble in hot water than in cold.

2.3.5 Inorganic fillers and Pigments [9,10]

Inorganic fillers and pigments may be added to a latex in order to cheapen and stiffen the product, or to color it. An ancillary effect, which may be exploited, is the effect of such fillers upon flow behavior. It must be emphasized, however, that no effects analogous to the reinforcement of dry rubbers by certain inorganic fillers are observed when the same fillers are incorporated in latex compounds. Thus carbon black and fine-particle kaolinite clays do not enhance the tensile strength and tear strength of vulcanized latex deposits as they do for products made from dry rubber. This difficulty is associated with the absence of a mastication step in the case of latex products.

Kaolinite clays Of the inorganic fillers which are commonly incorporated in latex compounds. They are cheap materials of fine particle size. They are readily dispersed in water with the aid of small amounts of dispersing agents; indeed some grades may be added dry to well-stabilized latex compounds.

Kaolinite clays may be added to natural rubber latex to the extent of 400 parts per 100 parts of rubber. At these levels the products are very hard and show virtually no rubbery characteristics. In low proportion (up to 30 parts per 100 parts of rubber), soft vulcanizes are obtained which have an increased tension set.

Calcium carbonates This group of fillers are included the various whittings, chalks and limestones. All are very cheap and all give poor quality products with a marked tendency to discoloration.

White pigments The most effective white pigment available for latex work is rutile titanium dioxide. The anatase type may also be used. For rubber latex work additions are usually of the order of 5 parts per 100 parts of rubber. For use in latex paints the proportion is often much higher.

2.4 Preparation of Dispersion [9,11]

With a few exceptions, compounding ingredients are added to latices as dispersions, according to the fact that they are water-insoluble solids.

Three important general principles regarding dispersion for addition to latices must be enumerated at the outset:

- i) The particle size of dispersions, as far as possible, may be comparable with that of the latex to which they are to be added.
- ii) The stability of dispersions should be comparable with that of the latex to which they are to be added. Furthermore, it is desirable that the stabilizing systems should be similar, otherwise untoward interaction effects may occur.
- iii) The pH of dispersions should be adjusted to that of the latex to which they are to be added. In this way the minimum of disturbance to the prevailing acid-base equilibrium occurs during the compounding.

2.4.1 Grinding equipment

The general method for preparing dispersions for latex work is first to make a coarse slurry of the powder with water which contains small amounts of dispersing agent and stabilizer, and then to grind the slurry in a suitable mill to produce a dispersion of small particle size.

The pieces of grinding equipment in common use fall into two categories:

- i) Those which merely break down aggregates of fine particles but do not effect any reduction of ultimate particle size. Pieces of equipment in this category are usually known as *colloid mills*.
- ii) Those which do affect a reduction of ultimate particle size as well as dispersing any agglomerates which may be present. Under this heading are to be included such items of equipment as *ball and pebble mills, ultrasonic mills, and attrition mills*.

2.4.2 Formulations for dispersions [9,11]

Attention is drawn to the following points specifically:

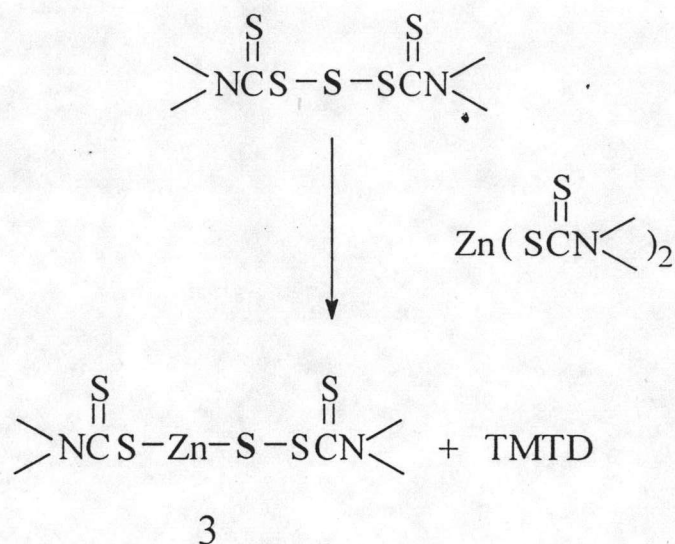
- i) The proportion by weight of active ingredient in a dispersion should always be simple integral sub-multiple, e.g. $\frac{2}{3}$, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, so that the conversion of active ingredient weight to requisite dispersion weight can be effected as simply as possible. The actual total solids content of the dispersion is largely incidental.
- ii) The general procedure for making up dispersion slurries is to combine the solutions of dispersing agents and stabilizers with the water, and then add the dry powder with high speed stirring.

iii) Accelerator dispersions may be prepared at 50% concentration if desired, but some, notably zinc diethyl dithiocarbamate, are rather prone to flocculate at this concentration. Consequently the proportion of accelerator may with advantage be reduced to 33%. Even so, it may be desirable to add a small amount of a hydrophilic colloid, e.g. 1% of methylcellulose, to enhance the stability of the dispersion and to discourage sedimentation.

2.5 Direct thiuram vulcanization of natural rubber [12,13]

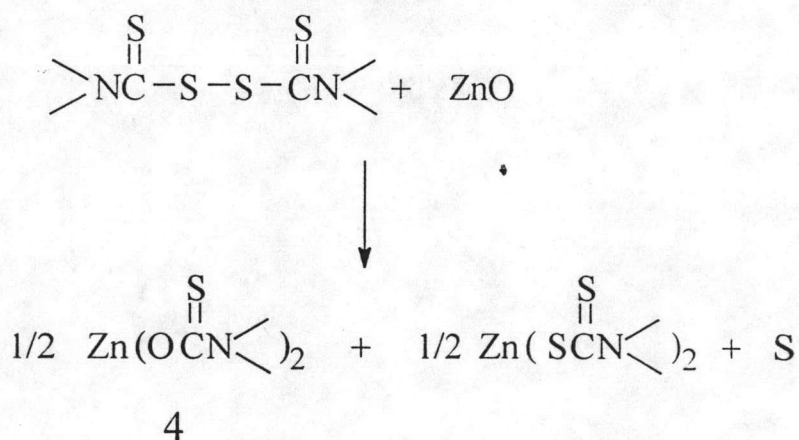
In the following, "direct" thiuram vulcanization will be understood as the vulcanization of natural rubber using N,N'-tetrasubstituted thiuram disulfides (TD). Vulcanization has been studied many times in the past from technology. The crosslinking in every case is connected with the presence of zinc oxide.

Thiuram disulfides, such as N,N,N',N'-tetramethyl thiuram disulfide. TMTD, along with zinc oxide are known to cure rubber without the addition free sulfur. The reaction between zinc oxide and TMTD, which generates sulfur for crosslink formation, is shown in Scheme 1. Studies in natural rubber indicate that the perthiodithiocarbamate anion, 1, which forms initially, does not liberate free sulfur but instead reacts with another molecule of TMTD to form the thiuram trisulfide, 2. The dithiocarbamate ion, which is liberated in the process, becomes zinc dithiocarbamate (ZnDTC).



Scheme 2

This complex is considered to be the active species which causes vulcanization to occur. Thiuram disulfide is regenerated during the exchange and reacts with zinc oxide to liberate more sulfur. Overall one-half of the thiuram disulfide is converted into ZnDTC. The remaining half produces zinc thiocarbamate, 4, and one atom of sulfur as shown in Scheme 3.



Scheme 3

2.6 Literature Review

J.G.Ameen, G.V.Elmore and A.E.Peter[14] studied the strippable solder mask material composed of three basic ingredients. A principal ingredient is polysulfone which is a thermoplastic, thermostable strippable base material. A second ingredient is a solvent for the polysulfone such as chlorobenzene, orthodichlorobenzene, methylene chloride or trichloroethylene. Chlorobenzene and orthodichlorobenzene are preferred solvents because of their higher boiling points. The third ingredient in the basic mask material is a filler necessary to hold the polysulfone in place during the soldering operation. This is due to the fact that at the elevated temperatures encountered during soldering, the polysulfone is in a molten state. Typical fillers which can be used are zinc oxide, calcium carbonate or finely divided particles of silicon dioxide. After the soldering operation, the mask material can be removed by soaking module in methylene chloride followed by a trichloroethylene vapor degreasing.

K.F.Drain, R.Summers and L.A.Nativi[15] 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 monomers have sufficient cohesion strength to allow them to be stripped into a single piece. The use of vinyl stearate monomer or high levels of filler (e.g. a fumed silica) in order to reduce the adhesion of the cured monomers. The suitable adhesion in

tensile shear mode is between 5-55 psi. This level of adhesion is sufficient to prevent ingress of solvent solder, plating or coating materials but low enough to allow easy dry stripping mechanically or by hand.

T.Matynia, R.Kutyla, K.Bukat and B.Pienkowska[16] studied properties of solder masks, hardenable in ultraviolet radiation, based on acrylate and methacrylate oligomers. Masks obtained with the use of epoxymethacrylate oligomers were of high viscosity, unstable in time, and readily gelating, which resulted in bad printability. 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 compositions viscosity decreased (from 290,000 to 60,000 cP) and their good printability was obtained. The addition of each kind of photoinitiator does not affect mask printability. The amount in a small range of 2-4% affect the mask adhesion to the surface and resistance to soldering. The mask containing 3% of the photoinitiator shows sufficient adhesion to copper and studies of resistance to soldering did not show changes on the surface in the form of blisters. The addition of fillers is closely connected with mask printability and its thermal resistance. The amount of fillers would be in range between 23-35%.

G.R.Unruh[4] studied the composition for providing ultraviolet curable temporary solder mask which included a) a photoinitiator, b) an antioxidant, c) a reactive diluent monomer capable of polymerization, and d) a thickener. Solder mask in this work is not carried in a solvent, therefore there are minimal health and environmental concerns. Also, this invention may 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.

This general composition may comprise the following ingredients in the percentages indicated in Table 2.3.

Table 2.3 General composition of ultraviolet curable temporary solder mask.

Ingredient	Effective % by weight
Reactive diluent monomer	5-90
Thickener	1-15
Antioxidant	0.01-2
Photoinitiator	1-10

The reactive diluent monomer of the above composition may be a substituted vinyl monomer, including tetrahydrofurfuryl-methacrylate, tetrahydrofurfurylacrylate, allyl methacrylate, n-alkyl methacrylate (C_2-C_{18}), 2-ethoxyethyl acrylate, isodecyl methacrylate, lauryl methacrylate, etc. The antioxidant includes naphthoquinone, benzoquinone, alkyl or aryl-substituted naphthoquinone or alkyl or aryl-substituted benzoquinone. The photoinitiator includes substituted benzophenones or substituted thioxanthenes. The suitable thickening agents include silicon dioxide, xantham gum, or acacia gum, carboxymethylcellulose, carboxyethylcellulose, attapulgite clay and similar compositions thereto.

T.Maeda, Y.Sasagawa, Y.Ikeda and T.Hiraharu[17] studied that water-based maskant composition comprises 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 per 100 parts by weight (as solids) of the latex constituent. The thickener includes carboxymethylcellulose, polyvinyl alcohol, crosslinking type acrylic emulsion. The amount of the thickener used is 0.1-10 parts by weight, preferably 1-3 parts per 100 parts by weight (as solids) of the latex constituent. The tensile strength and elongation of a film obtained from the composition are 50-150 kgf/cm² and 100-800%, respectively.