

الإجابة النموذجية لإمتحان كيمياء تكنولوجيا البويات

416ك

(ورقة امتحانية كاملة)

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الشعبة : الكيمياء و الكيمياء التطبيقية

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قسم : الكيمياء

كلية : العلوم

## Model Answer

1 - a) Write short notes on the types of solvents used in paints, and illustrate what its importance.

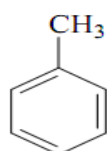
### Answer

The solvents generally used in the paint industry may be divided into three classes:

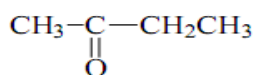
- a. Hydrocarbon solvents
- b. Oxygenated solvents
- c. Water

Hydrocarbon solvents are the most commonly used solvents in paints to carry the pigment and binder. They are divided into three groups: aliphatic, naphthenic, and aromatic. The preferred type of solvent is an odorless aliphatic hydrocarbon (mineral spirits), which can be used in all areas including home. However, mineral spirits do not dissolve all binder resins. Aromatic solvents provide stronger solvency, but with a greater odor. The most common are toluene, xylene, and naphthas. The principal oxygenated solvents are ketones, esters, glycol esters, and alcohols. They offer much stronger solvency and are widely used as active solvents synthetic binders.

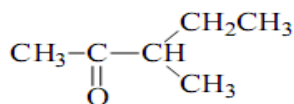
Water is the main ingredient of the continuous phase of most emulsion paints. The advantages of water as a solvent are its availability, cheapness, lack of smell, nontoxicity, and nonflammability. However, it is not an ideal paint solvent because of its limited miscibility with other organic solvents, and because film formers designed to be dissolved or dispersed in water usually remain permanently sensitive to water. Some examples:



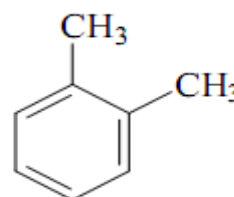
toluene



methylethyl ketone



methyl isobutyl ketone



xylene

Their importance:

1. Regulate application properties
2. Control consistency and character of finish (minimizes defects)
3. Control evaporation rate
4. Adjust solids level that influence film application thickness
5. Adjust and influence coating viscosity (thickness of paint)
6. Are used in resin manufacturing

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**b) Write the drying mechanism of the following coatings:**

**i- Oil based coatings.**

**ii- Polyurethane coatings.**

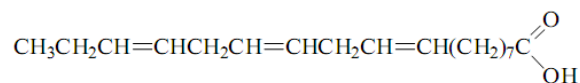
**Answer**

**i- Oil based coatings:**

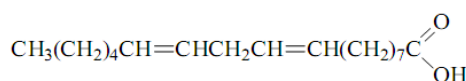
**Composition.** Oil-based paints (oil paints) are among the oldest organic coating materials; they have been known for more than 2000 years. Oil paints consist of natural drying oils (e.g., linseed oil, China wood or tung oil, and soybean oil) which undergo autoxidative polymerization in the presence of catalytic driers and atmospheric oxygen. Further constituents may include hard resins (e.g., alkylphenolic resins) that generally react with the drying oils at elevated temperature (230-280°C) to form oleoresinous binders. On account of the air sensitivity of the oils, heating mainly takes place under an inert gas atmosphere.

The thickness of an oil-paint coating is restricted on account of the atmospheric oxygen required for curing.

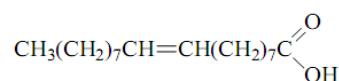
Linseed oil is a mixture of triglycerides of long chain carboxylic acids. Some of the major component carboxylic acids are:



linolenic acid  
(cis, cis, cis -9, 12, 15 - octadecatrienoic acid C<sub>18</sub>H<sub>30</sub>O<sub>2</sub>)



Linoleic acid  
(cis, cis -9, 12 - octadienoic acid C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>)



Oleic acid  
(cis, -9, - octadecenoic acid C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>)

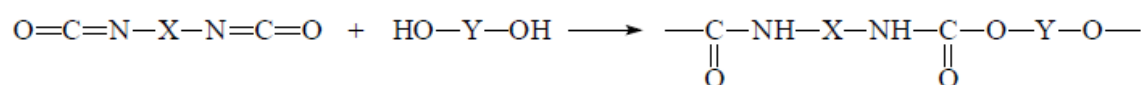
During film formation (curing), atmospheric oxygen reacts with the oil to form hydroperoxides which decompose into radicals and then initiate polymerization of the binder. Driers (metallic soaps such as cobalt, lead, and manganese naphthenates or



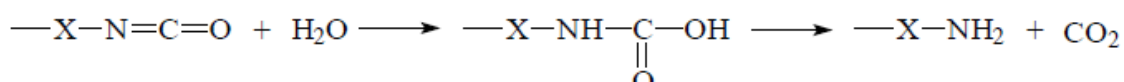
(e.g., hydroxyl groups) for chemical hardening (curing). However, this term now includes a large variety of binders. Polyurethane paint films all have a polymeric structure with urethane, urea, biuret, or allophanate coupling groups. Coupling can occur during paint hardening (curing) as the result of polyaddition of relatively low molecular mass starting products.

Polyurethane coating resins and varnishes offer advantages over alkyd resin systems in speed of drying, hardness of the film and resistance to wear. Types made in New Zealand include urethane oils, urethane alkyds, moisture curing polyurethanes and foams.

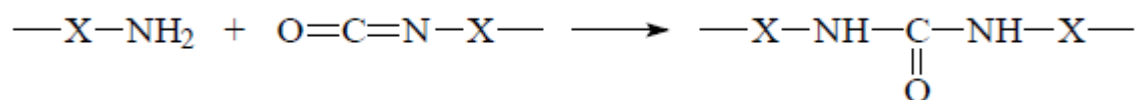
A polyurethane is formed by the reaction of a polyalcohol and an organic di-isocyanate:



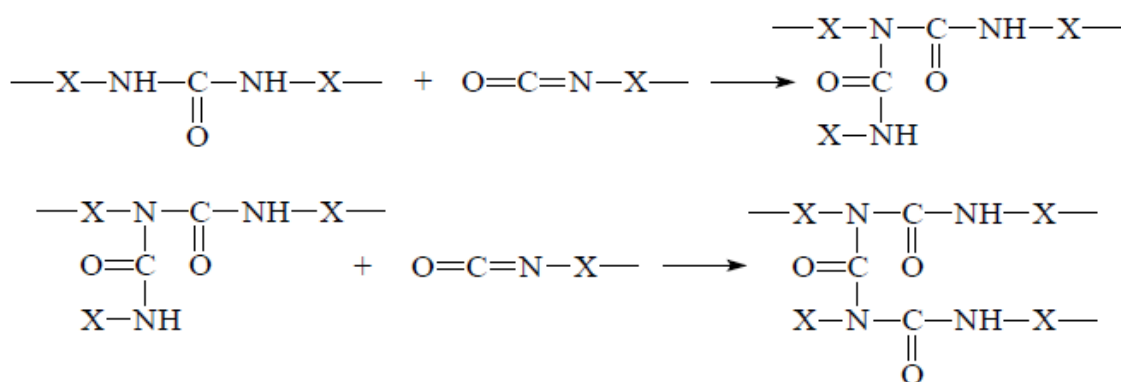
When isocyanates react with water, amines and carbon dioxide are produced:



The amine can then react with the isocyanate to form a "disubstituted urea":



This can then react with further isocyanate to give crosslinks between the polyurethane chains, giving a durable resin:



**2 a) How can we decrease the environmental pollution of alkyd resins.**

Answer

This can be done by decrease the using of organic solvents and this can be done by two ways :

**First way** by dissolving it in water by converting it to waterborne alkyd resins by:

1) Alkyd resins with high acid numbers ( $> 50$ ) are neutralized with amines (normal air-drying resins have an acid number  $< 10$ , oven-drying resins 20-35); solubility in water is due to salt formation

2) Alkyd resins are emulsified in water after addition of emulsifying agents and stabilizers or after chemical modification with special monomers e.g. polyglycols.

**Second way** by using Alkyd Resins with High-Solids Paints. High solids content can be obtained in three ways:

- Use of solvents with stronger solvent power, so that resin solutions with lower viscosities are obtained with **less** solvent. This method is used for stoving paints based on conventional alkyd-melamine resin combinations; it can also be applied with certain restrictions to air-drying systems.
- Use of reactive diluents that are incorporated into the film by condensation when the stoving paints harden.
- Use of low-viscosity, reactive alkyd resins that have a lower solvent requirement than conventional products.

**b) Write short notes on:**

i- Acrylic coatings.

ii- Light stabilizers

### Answer

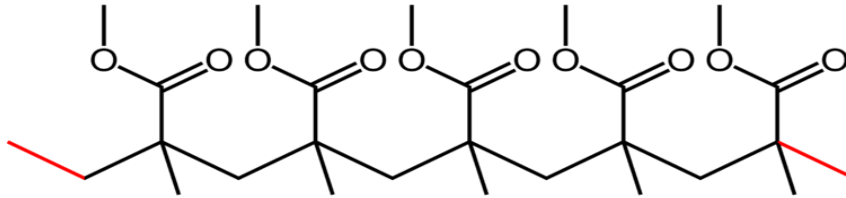
#### **i- Acrylic coatings:**

Polyacrylates as binders consist of copolymers of acrylate and methacrylate esters. Other unsaturated monomers (e.g., styrene and vinyltoluene) may also be incorporated, but usually to a lesser extent. Copolymers formed exclusively from acrylates and/or methacrylates are termed straight acrylics.

***Acrylate resins have several advantages over other paint binders :***

- 1) Polyacrylates are only slightly attacked by chemicals, and confer a high degree of resistance to paints
- 2) Polyacrylates are colorless, transparent, and do not yellow, even after prolonged thermal stress
- 3) Polyacrylates do not absorb above 300 nm and are therefore not degraded by UV radiation (as long as they do not contain styrene or similar aromatic compounds).

- 4) Polyacrylates do not have unstable double bonds
- 5) Polyacrylates have outstanding gloss and gloss retention
- 6) Acrylates, and especially methacrylates are stable to hydrolysis long as they do not contain styrene or similar aromatic compounds)



**Skeletal formula of a short length of a polymethyl methacrylate chain**

### ii- Light stabilizers:

High-quality industrial coatings, especially automotive finishes, are subjected to severe weathering in exterior applications. In two-coat metallic coatings, exposure to UV light, oxygen, moisture, and atmospheric pollution causes decomposition of the polymer material in the automotive finishes. This decomposition results in loss of gloss, crack formation, color changes, and delamination phenomena.

High-energy UV light is particularly detrimental because each polymer material can be damaged particularly easily at one or more wavelengths in the UV range.

Light stabilization is therefore essential.

**Methods of Stabilization.** Two stabilization methods have been adopted industrially:

1. Competitive UV absorption by UV absorbers in the wavelength range 290-350 nm
2. Trapping of the radicals formed during polymer degradation by radical scavengers (hindered amine light stabilizers, HALS)

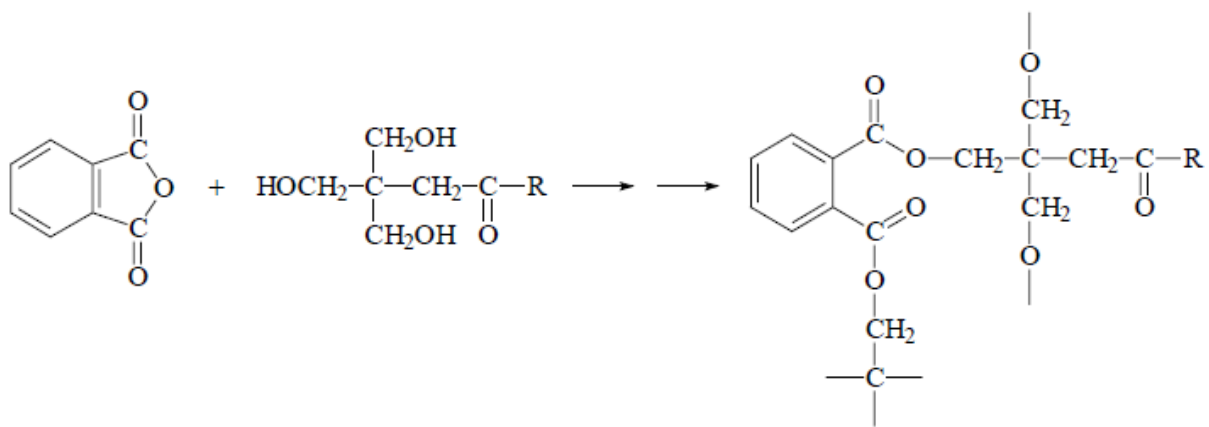
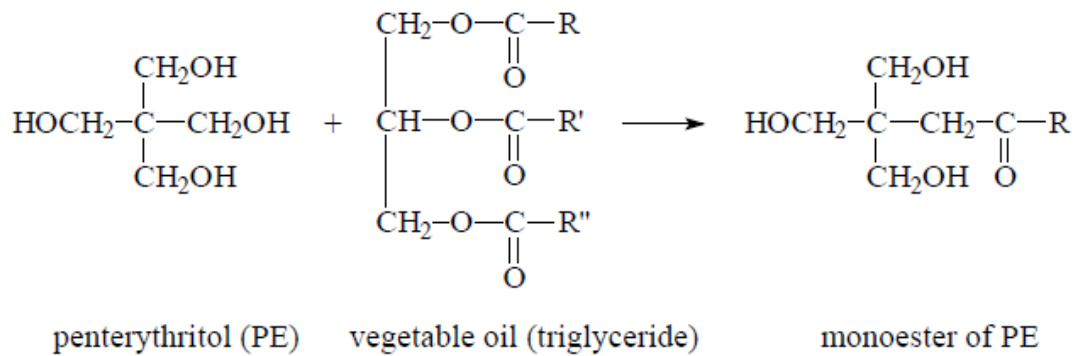
### 3- a) Discuss the two stages for the manufacture of alkyd resins.

#### Answer

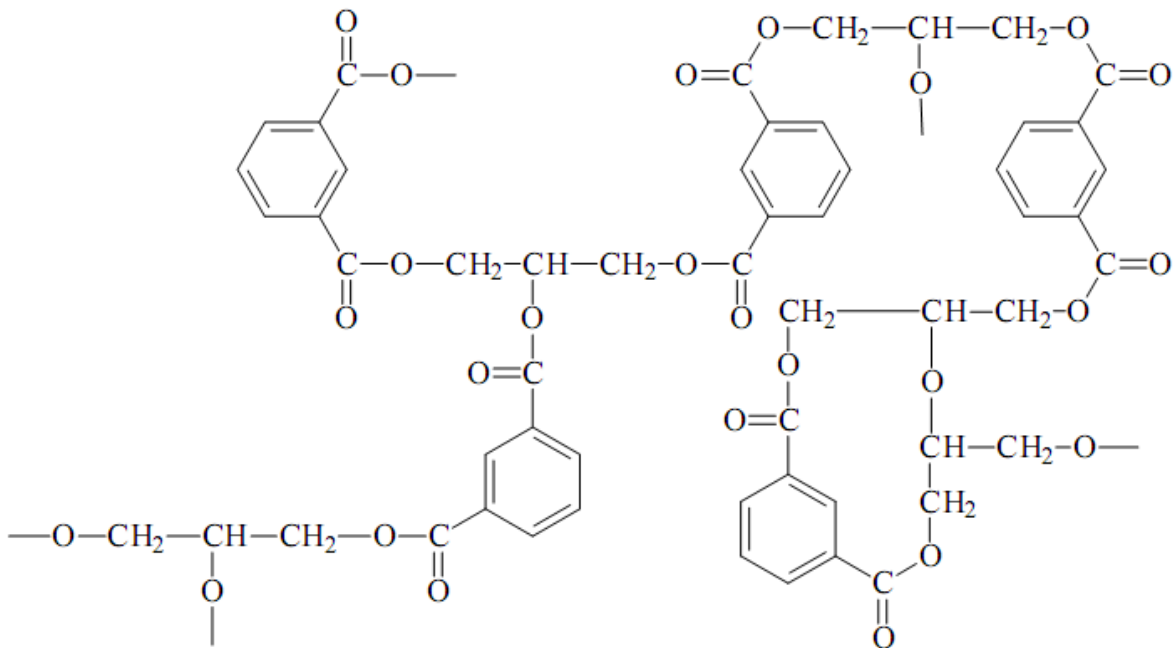
#### The manufacturing process:

The manufacture of the alkyds proceeds in two stages. Pentaerythritol and vegetable oil are first heated with the catalyst for about two hours at 270°C. The vegetable oil is an ester of glycerol and long chain unsaturated fatty acids, and the reaction is a transesterification, the fatty acids forming an ester with the polyhydroxy-alcohol pentaerythritol. Di- and tri- esters of PE and di- and monoglycerides are also presumably formed. After cooling the mixture to 150°C, a slight excess of phthalic anhydride is added and the mixture

is reheated to 240°C where it is held for several hours while the polyester alkyd resin is formed:



A portion of the complex glyceryl phthalate resin would look as follows:



The reaction is monitored by acidity and viscosity measurements. Water is removed by evaporating with the solvent which is recycled. The unsaturated fatty acid residues react with oxygen to give further polymerisation in the drying of the paint or curing of the resin. By changing oil, acid or alcohol, a wide range of alkyd resins can be made.



**b) Write short notes on the paint formulations.**

**Answer**

The formulation of a paint is a matter of the skill and experience of a paint technologist. It is largely determined by the ratios of the constituents in paints and the nature of the substrate to which the paint is to be applied. Once the proper constituents of a paint have been selected, these materials are combined together in the proper amounts. The fundamental parameters used in the formulation of a paint are :

- a. pigment to binder ratio.
- b. solid contents.
- c. pigment volume concentration.
- d. cost.

The performance capability of a paint depends largely on the capability of a binder in the film to provide a completely continuous matrix for the pigment. Thus, the weight ratio of the pigment and extender content to that of binder solid content can be usefully correlated with the performance properties of a paint. The total solid content of a paint is another simple property that can be readily determined from a percentage weight formula. This is the amount of material that does not evaporate during the formation of a paint film on a surface representing the pigments and binder solids.

The concept of pigment volume concentration (PVC) is of far-reaching consequences for the modern paint formulator. It is defined as the percentage of pigment volume in the total volume of solids in the paint.

$$\text{PVC}\% = \frac{\text{Volume of Pigment} \times 100}{\text{Volume of Pigment} + \text{Volume of Nonvolatile Binder}}$$

However, the requirements of high gloss, high opacity, and high durability are found to be of conflicting nature as maximum gloss and durability are achieved at low PVC, and maximum opacity at either moderate or very high PVC. The following tabulation is used by some paint manufacturers as an approximate range of PVC for a given paint:

This level of pigmentation is known as the critical pigment volume concentration (CPVC). CPVC is usually described as the PVC at which there is precisely the right amount of binder to wet the pigment particles and to fill the voids between them.

**4- a) Alkyd resins can be divided into different types. (Discuss)**

**Answer**

According to the oil or fatty acid content, and its types the alkyds are divided into three broad categories:

- Short oil (to 40 percent)
- Medium oil (40-60 percent)
- Long oil (more than 60 percent) alkyd resins

They are further divided into drying (oxidizing) and nondrying (nonoxidizing) types.

Nondrying oil alkyds do not readily form films and, as such, they are mainly used as plasticizers for other binders.

Drying oil alkyds can form films (coatings) through oxidative polymerization in a similar manner to that of the natural oils (linseed or soya) from which they are made.

**Short** drying oil alkyds are typically made of linseed, soya, or dehydrated castor oils. The linseed based alkyds are used in automotive refinishing enamels and in general purpose air drying enamels.

Nondrying, short oil alkyds are generally based on castor or coconut oils. They are used with nitrocellulose for exterior lacquers. Coconut oil alkyds give the best exterior durability; castor oil lacquers have the best film properties.

**Medium** oil linseed and soya alkyds are used in automotive refinishing and implement enamels. In general, all-round durability of medium oil alkyds are better than their longer or shorter relations.

**Long** oil length alkyds are almost always prepared from drying and semidrying oils, with pentaerythritol being the preferred polyol. The most common oils used are linseed and the semidrying oils, soya, safflower, sunflower and tall oil. Their main use is in architecture and maintenance as brushing enamels, undercoats, and primers, and also marine paints. Their slowness to dry and lack of response to forced drying has prevented their use in industrial finishes.

**b) Illustrate the important types of paint systems.**

**Answer**

**1. Solventborne Paints:**

Paints and coating materials normally consist of a physical mixture of binders, pigments, extenders, additives, and solvents. Depending on the method of application and area of use, the solids content may reach 80 wt%, the proportion of pigment may reach 60% of the solids content. The technologically most important component is the binder (or binder mixture). Binders may be classified as physically or chemically drying according to their film-forming mechanism.

Physically drying paints are solutions of thermoplastic polymers with molecular masses exceeding 20000; on account of their low solubility they have a high solvent content (> 60%) and a low solids content. Chemically drying paints have a fairly low solvent content (30-60%) and a high solids content because the polymer network is formed by cross-linking of the binder ( $M_n$  800- 10000) usually at elevated temperatures or via radiation to form thermosetting coatings. Oxidatively drying paints contain allyl groups and reactive double bonds, and cross-link by absorbing oxygen and forming ether bridges.

Since the beginning of the 1980s environmental requirements have become increasingly important for two main reasons, especially in the case of paints with low material transfer (application) efficiencies :

- a. Avoidance of the use of toxic, carcinogenic, mutagenic, or teratogenic organic solvents.
- b. Drastic and in some cases legally imposed reduction of solvent contents

Typical examples of low-solids paints (solvent content usually > 60 wt O h ) are:

- 1) Metallic (effect) base paints for mass production of automobiles and touch-up finishes
- 2) Thermoplastic coatings
- 3) Coatings for the electronics and optoelectronics industries

**2. Waterborne Paints:**

Waterborne (water-thinnable) paints were developed in the 1950s with the aim of replacing the common organic paint solvents by water, which has the obvious advantages of being noncombustible and nontoxic.

Waterborne paints provided the technological basis for electrodeposition paints

, in which negatively charged paint particles (anaphoresis, industrial introduction at the beginning of the 1960s), or positively charged paint particles (cataphoresis, industrial introduction at the end of the 1970s) are deposited from aqueous solution onto metallic substrates by application of an electrical field. With the scarcity of raw material resources (eg , petroleum) and the introduction of more stringent environmental legislation, waterborne paints were developed on a broader basis during the 1970s (e.g., as spraying and dipping paints). Among those coating materials that can be classed as environmentally friendly, waterborne paints have the widest potential as regards application, drying methods, and industrial uses.

### **3. Solvent-Free and Low-Solvent (High-Solids) paints:**

Solvent-free and low-solvent paints are a development of conventional high-solvent paints and are formulated to comply with increasingly stringent environmental requirements. In this section only those liquid coating materials are discussed that can be applied by conventional methods (coating, spraying, rolling, dipping, and pouring).

There are several reasons for developing solvent-free and low-solvent paints :

- 1) Reduction of atmospheric pollution
- 2) Savings in materials and transportation costs
- 3) Savings in energy costs involved in paint production and use
- 4) Time savings due to higher layer thicknesses per application cycle
- 5) Improvement in safety due to low-solvent content

The advantage of high-solids paints compared with more recent technologies lies in the fact that they can be produced and applied with conventional equipment and by well-known methods. Consequently potential users are primarily small and mediumsized paint shops, the maintenance and architectural sector, as well as the do-it-yourself sector.

### **4. Coating Powders:**

Coating of substrates (particularly metallic substrates) with particulate plastics is a well-established technology. The fluidized-bed process was developed in 1952. The electrostatic powder coating technique introduced in 1965 has, however, made a substantially greater impact.

Thermosetting coating powders are applied mainly by electrostatic spraying and dominate the market.

**5- a) Surfactants are very useful compounds and used in different industries in our life, illustrate its importance in coating industry.**

**Answer**

**Surfactants were used in different ways in the paint additives such as:**

**1. Defoamers:**

Foam may occur as an interfering factor during paint production. Liquid foams are a fine distribution of a gas (normally air) in a liquid. Thin films of liquid (the lamellae) separate the gas bubbles from one another and the gas- liquid interfacial area is quite high. Pure liquids do not foam; surface-active materials must be present in order to obtain stable foam bubbles.

**2. Wetting and Dispersing Additives:**

In the production of pigmented paints, the pigment particles must be distributed as uniformly and as finely as possible in the liquid phase. The pigment agglomerates must first be wetted by the binder solution. This process mainly depends on the chemical nature of the pigments and binders and can be accelerated by using wetting additives.

**Dispersing additives** are stabilizing substances that are adsorbed onto the pigment surface via pigment-affinic groups (another groups with a high affinity for the pigment surface) and establish repulsive forces between individual pigment particles. Stabilization is achieved either via electrostatic charge repulsion or via steric hindrance due to molecular structures that project from the pigment surface into the binder solution.

**3. Surface Additives:**

Many surface defects can be explained by differences in interfacial tension. Poor substrate wetting, for example, must be expected if the paint has a higher surface tension than the substrate to be coated. When spray dust or solid dust particles fall onto a freshly coated surface, craters are formed if the deposited droplets or particles have a lower surface tension than the surrounding paint material. Craters are also formed if the surface to be coated is locally contaminated with substances having a very low surface tension (e.g., oils) and the surface tension of the paint is too high to wet these contaminated areas.

**b) Discuss in brief the wetting and dispersing additives.**

**Answer**

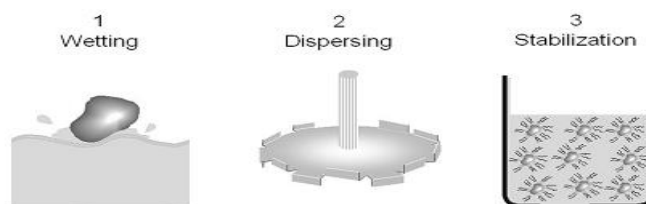
In the production of pigmented paints, the pigment particles must be distributed as uniformly and as finely as possible in the liquid phase. The pigment agglomerates must first be wetted by the binder solution. This process mainly depends on the chemical nature of the pigments and binders and can be accelerated by using wetting additives.

If this pigment grinding step is not optimized, then a wide variety of defects can occur:

- Flocculation
- Gloss decrease
- Color shift
- Flooding/floating
- Settling
- Viscosity instabilities

**The Dispersing Process:**

The various processes which occur during pigment grinding can be divided into the following three steps:



**During Step 1 (Wetting)**, all of the air and moisture at the pigment surface is driven off and then replaced by the resin solution.

**Step 2 (Grinding)** represents the true pigment grinding stage. Through mechanical energy (impact and shear forces), the pigment agglomerates are broken up and accordingly reduced in size.

In the concluding **step 3 (Stabilization)**, the pigment dispersion must be stabilized in order to prevent the formation of uncontrolled flocculates.

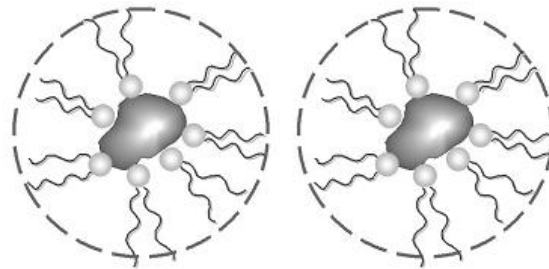
Steps 1 (wetting) and 3 (stabilizing) can be influenced by additives. Wetting additives accelerate the wetting of pigment agglomerates by the resin; dispersing additives improve the stabilization of the pigment dispersion. One and the same product can oftentimes function as both the wetting and the dispersing additive.

Wetting additives are materials of low molecular mass with a typical polar-nonpolar surfactant structure; they reduce the interfacial tension between the binder solution and the pigment surface. Wetting additives can be defined as substances which are designed to

reduce interfacial tension and which, as a result, increase the “spreading pressure“ so that the wetting process is accelerated.

Characteristic for such substances is their surface-active structure: polar, hydrophilic structural elements along with nonpolar, hydrophobic structural elements combined in one molecule. Wetting additives can be classified as either ionic or non-ionic - according to the chemistry of the polar segment in the molecule. The nonpolar segment is, as a rule, represented by hydrocarbon chains.

**Dispersing additives** are stabilizing substances that are adsorbed onto the pigment surface via pigment-affinic groups (another groups with a high affinity for the pigment surface) and establish repulsive forces between individual pigment particles. Stabilization is achieved either via electrostatic charge repulsion or via steric hindrance due to molecular structures that project from the pigment surface into the binder solution. The first mechanism is prevalent in waterborne emulsion systems, the latter predominates in solvent borne paints. In coatings with water-soluble resins both mechanisms are equally important.



Steric stabilization of pigment particles to avoid flocculation

Since most paints contain more than one pigment, the pigments often segregate in the paint film during drying. Nonuniform pigment distribution within the film surface is termed flouting. In flouting the surface is uniformly colored, concentration and thus shade differences occur only perpendicular to the surface; this phenomenon only becomes evident in the rub-out test.