Benha University	**Chem. & Tech. of paints 416**	**Time: 2 hrs.**
Faculty of Science	**Chem.**	**Summer 2016**
Chemistry Department	**4th year students**	

Answer four questions only:

1 – a) Write the drying mechanism of the following coatings: *(6 Marks)*

i- Oil based coatings.

ii- Polyurethane coatings.

Answer

i- Oil based coatings:

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.

Auxiliaries may be added to oil paints to improve their wetting and flow properties. The desired handling consistency is generally adjusted with aliphatic hydrocarbon solvents such as mineral spirits and in certain cases with toluene or xylenes. With clear varnishes 5- 10 wt% of solvent is sufficient, with paints 10-20 wt% is sufficient. There are very few restrictions in the choice of pigment; basic pigments (e.g., zinc oxide) can be used.

Conventional dispersion equipment (e.g., ball, roller, or sand mills) are suitable for producing oil paints.

Oil paints are relatively environmentally friendly as long as hazardous solvents and toxic pigments (e.g., red lead or zinc chromate) are not used. The oils used in such paints have a low viscosity. They are therefore particularly suitable for priming coats on manually derusted steel surfaces since they wet and penetrate the residual layers of rust well, resulting in thorough coverage. Oil paints are easily applied by conventional methods (e.g., brushing, roller coating, spraying, and dipping).

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 octoates) catalyze formation and decomposition of the hydroperoxides and thereby accelerate film formation. A combination of several driers is normally used to control the curing reaction at the surface and in the interior of the coating.

The drying process is a complex one of polymerisation, probably catalyzed by peroxides.

ii- Polyurethane coatings.

Polyurethanes result from the reaction of a polyalcohol and an organic di-isocyanate. They can be used as surface coatings, to make furniture and footwear and in foam form, for packaging.

The term polyurethane paints (coatings) originally referred to paint systems that utilized the high reactivity of isocyanates groups with compounds containing acidic hydrogen atoms (e.g.,

hydroxyl groups) for chemical hardening (curing). However, this term now includes a large variety of binders. The amount of

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.

The manufacture of condensed polyurethanes

Urethane oils can be formed by the addition of vegetable oil to the polyurethane. Urethane alkyds can be formed by reacting isocyanates with alkyds. They cure in the same way as alkyds, that is, by oxidative crosslinking of the unsaturated groups in the fatty acid portions of the molecule.

Moisture curing polyurethanes are produced by reaction of isocyanates with polyether or polyester polyols. Unreacted isocyanate groups are present and these react with atmospheric moisture to cure the resins by forming crosslinked polyurea polyurethane structures.

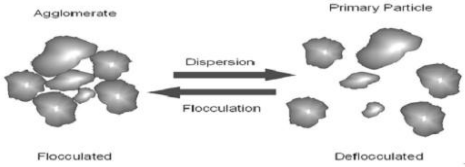
b) Write short notes on: *(6Marks)*

i- 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.

The Dispersing Process:

Interactive forces between the particles are relatively small so that such forces can be overcome by traditional dispersing equipment. In the dispersing phase, energy is added to the system and therefore smaller particles (with a larger interface to the resin solution) are formed.



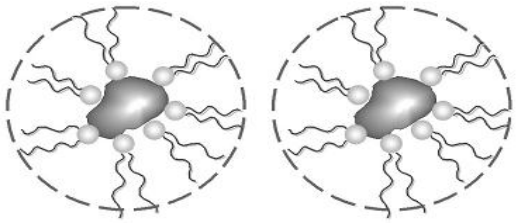
The various processes which occur during pigment grinding can be divided into the following three steps:

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.

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.



Steric stabilization of pigment particles to avoid flocculation

Wetting and dispersing additives can also solve flooding and floating problems.

ii- Types of solvents used in paint industry.

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

a. Hydrocarbon solvents : 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.

b. Oxygenated solvents: The principal oxygenated solvents are ketones, esters, glycol esters, and alcohols. They offer much stronger solvency and are widely used as active solvents for synthetic binders. Ketones are characterized by their strong odor, range of water solubility, and evaporation rate. Esters provide solvency nearly equal to ketones but with more pleasing odors.

c. Water: 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 no flammability. 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.

2–a) Discuss the preparation of each of the following binders: ***(6 Marks)***

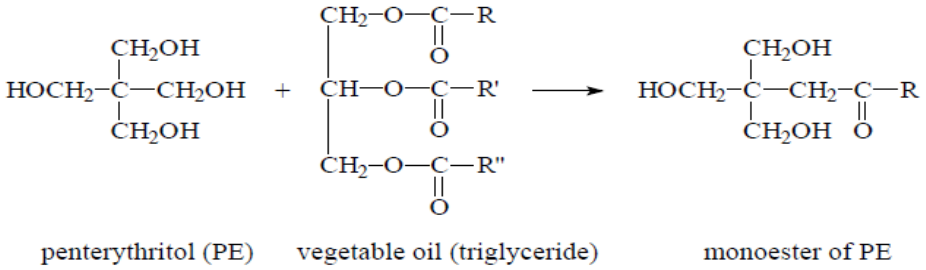
i- Chlorinated Rubber.

To manufacture chlorinated rubber (CR) natural or synthetic rubber such as polyethylene, polypropylene or polyisoprene is degraded to low molecular mass compounds by mastication or addition of radical formers and dissolved in carbon tetrachloride (CTC). Chlorine contents are typically 64-68 wt %. Chlorine gas is introduced into this solution and reacts with the raw material to form CR. The solution is then introduced into boiling water. The CR is precipitated, and the solvent vaporizes. The CR is separated from water, rinsed, dried and ground to form a white powder which is the saleable product. After removal of the water, chlorine, hydrochloric acid and other impurities the solvent is reused.

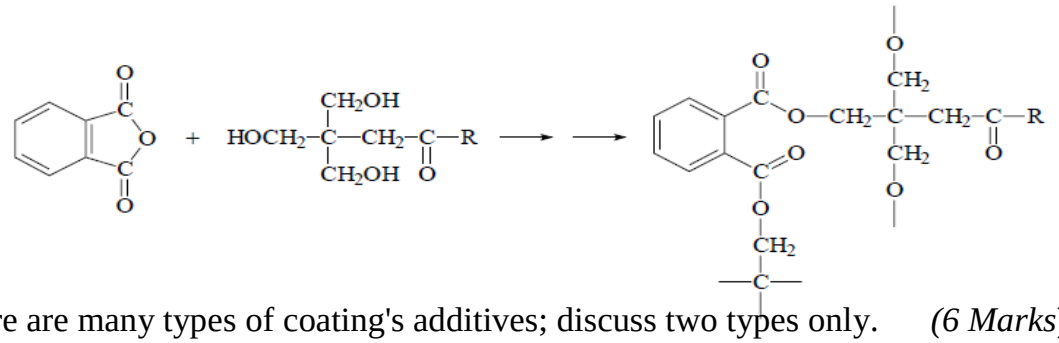
ii- Alkyd resins.

The manufacture of the alkyds proceeds in two stages. 1- Monoglycerolysis, Pentaerythritol and vegetable oil are first heated with the catalyst for about two hours at 270^{o}C. The vegetable oil is an ester of glycerol and long chain unsaturated fatty acids, and the reaction is a trans-esterification, 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.

2- Esterification, 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:



penterythritol (PE) vegetable oil (triglyceride) monoester of PE



b) There are many types of coating's additives; discuss two types only. *(6 Marks)*

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.

Silicone additives (mainly organically modified methylalkyl polysiloxanes) lower the surface tension of coatings and minimize surface tension differences.

Preservatives:

Paints, the liquid paint as well as the dry film, are easily attacked by microorganisms and therefore biocides/fungicides are used as protective means. Microbial growth in the liquid paint may cause gassing, bad odour, discoloration and can finally render the paint totally unusable. This is mainly a problem in aqueous systems; in solvent based coatings the organic solvents effectively protect the paint against microorganisms. When the dry film is attacked by mildew and fungi, this first of all detoriates the optical appearance of the surface but also the mechanical properties of the film are degraded.

3–a) What is the importance of pigments in paint composition? ***(3 Marks)***

Pigments are used in paint formulation to carry out one or more of the following tasks:

1. Provide color
2. Hide substrates and obliterate previous colors
3. Improve the strength of the paint film
4. Improve the adhesion of the paint film
5. Reduce gloss
6. Reduce cost

b) Classify the alkyd coatings. ***(3 Marks)***

According to the oil or fatty acid content, 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.

c) What is the importance of acrylic coatings? ***(3 Marks)***

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.

d) How can you determine the pigments volume concentration? ***(3 Marks)***

It is defined as the percentage of pigment volume in the total volume of solids in the paint.

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

4– a) Write short notes on: *(6Marks)*

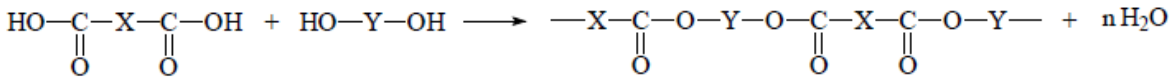
i- Unsaturated polyester resins.

These are formed from the reaction of a diol (a molecule containing several hydroxyl groups) and an unsaturated diprotic acid. The resulting polyester chains are dissolved in a reactive solvent. The chains crosslink to form a hard, strong resin which is used in making the hulls of boats and in the production of "synthetic marble".

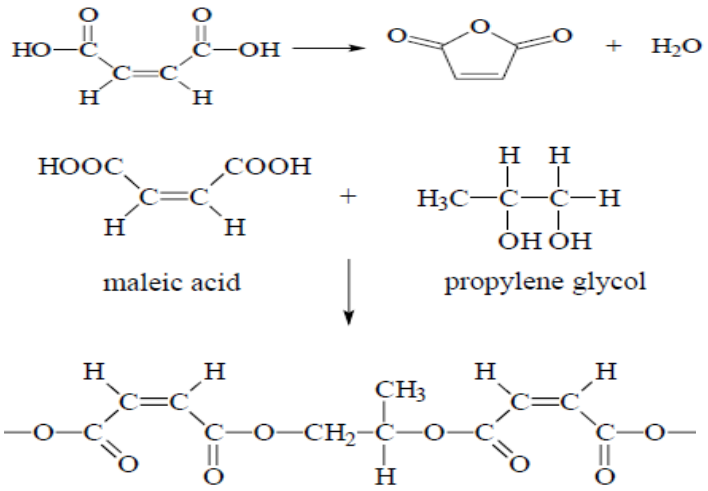
The coatings primarily contain monomers. In addition to styrene, the most frequently used monomer; it has become increasingly common in recent years to use acrylates as the copolymerisable monomers, especially in coatings for UV curing.

Coatings containing styrene cure in virtually any thickness as the styrene which initially acts as a solvent polymerises with the double bonds of the UP resin and is incorporated into the paint film.

In general, polyester resins result from the condensation reaction between a diprotic acid and a polyhydric alcohol, e.g.



Maleic acid is a diprotic carboxylic acid (i.e. it has two carboxylic acid groups) so in this case the two carboxylic acid groups of the same acid molecule react together to give the five membered ring of maleic anhydride as follows:



ii- Importance of solvents in paint industry.

In brief they

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

b) Discuss the efforts made to produce a waterborne alkyd. ***(6 Marks)***

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.

3) Alkyd Resins with High-Solids content. Alkyd resins have been developed for producing high-solids paints to reduce solvent emission.

5– a) Write short notes on paint formulation? *(6 Marks)*

The formulation of 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.

The fundamental parameters used in the formulation of paint are:

a. Pigment to binder ratio.
b. Solid contents.
c. Pigment volume concentration.
d. Cost.

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. It is an easily measurable and a helpful concept in paint formulation. In general, paints with a

pigment to binder ratio of greater than 4:1 are low gloss, suitable only for some interior applications.

The total solid content of 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.

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

The PVC offers a more scientific approach to the formulation of paints and its effects on important properties such as gloss, opacity, durability, rheology, and washability of paints.

b) Mention only the ways of paint drying take place. ***(3 Marks)***

Drying of the paint on the substrate takes place physically (1- 3) or chemically (4):

1) Evaporation of the organic solvents from solvent-containing paints
2) Evaporation of water from waterborne paints
3) Cooling of the polymer melts (powder coatings)
4) Reaction of low molecular mass products with other low or medium

c) Write short notes on the plasticizers. ***(3 Marks)***

Plasticizers are organic liquids of high viscosity and low volatility. The esters of dicarboxylic acids (e g, dioctyl phthalate) are well-known examples. Plasticizers work by embedding themselves between the chains of polymers, spacing them apart (increasing the "free volume"), and thus significantly lowering the glass transition temperature for the plastic and making it softer. Plasticizers lower the softening and film-forming temperatures of the binders. They also improve flow, flexibility, and adhesion properties. Chemically, plasticizers are largely inert and do not react with the binder components. Most binders used today are inherently flexible and can be regarded as "internally plasticized" resins. For this reason, use of plasticizers has declined.