

# PAINTS AND COATINGS

FORMULATION - TYPES  
PROPERTIES - USES

PH VALUE

1

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## PAINTS AND COATINGS

### ■ FORMULATION

- PAINT IS A LIQUID MATERIAL, WHICH, WHEN APPLIED TO A SUBSTRATE, FORMS A COHERENT AND ADHERING FILM

PH VALUE

2

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ MAIN TYPES:

- Solvent borne
- Solvent free
- Water borne
- Powder coatings

PH VALUE

3

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ MAIN COMPONENTS OF PAINTS:

- Binders
- Pigments
- Extenders
- Solvents
- Additives

pH VALUE

4

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ BINDERS

- binding the paints components together
- assure adhesion to substrate

The (main) binder type is designating the **generic** type of paint

pH VALUE

5

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ BINDERS

- PHYSICALLY DRYING:  
no chemical conversion, only evaporation of solvent
- OXIDATIVELY CURING:  
evaporation of solvent, then chemical conversion of binder, mainly through oxidation
- CHEMICALLY CURING:  
evaporation of solvent, then chemical conversion through reaction between components

pH VALUE

6

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## PAINTS AND COATINGS

PHYSICALLY DRYING:	Solution:	Tars, bitumens, chlorinated rubbers, vinyls, acrylics
	Dispersion:	PVAs, acrylics
OXIDATIVELY CURING:	Solution/ dispersion	Oil based, alkyds, modified alkyds, oleoresinous
CHEMICALLY CURING:	Solution/ dispersion/ 100% solids	Epoxyes, polyurethanes, zinc silicates, silicones

pH VALUE

7

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ PHYSICALLY DRYING PAINTS:

- CHLORINATED RUBBERS
- VINYLs
- ACRYLICS
- EPOXY ESTERS
- BITUMENOUS
- PVA
- LATEX

REDISSOLVABLE

pH VALUE

8

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ OXYDATIVELY CURING PAINTS:

- ALKYDS (incl. combinations):
  - URETHANE/ALKYD
  - SILICONE/ALKYD
  - ALKYD/PHENOLIC
  - ALKYD/PHENOLIC/TUNG OIL
- OIL BASED (incl. combinations):
  - URETHANE/OIL

REACTION WITH OXYGEN

pH VALUE

9

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ CHEMICALLY CURING PAINTS:

- EPOXY
- POLYURETHANE
- POLYESTER
- VINYL ESTER
- ACRYLIC/ISOCYANATE
- ZINC SILICATES

REACTION BASE  $\Leftrightarrow$  HARDENER  
ALMOST ALWAYS TWO- OR MULTI-PACK

pH VALUE

10

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ OTHER CURING MECHANISMS:

- MOISTURE CURING:
  - POLYURETHANES
  - POLYSILOXANES
  - ZINC ETHYL SILICATE
  - CEMENT BASED
- HEAT CURING:
  - SILICONES
- RADIATION CURING:
  - UV-CURED LACQUERS

pH VALUE

11

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ BINDERS - NATURAL RESINS

- asphalt/pitch/tar
- animal oils
- vegetable oils
- rosins
- natural latex

pH VALUE

12

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ BINDERS - SYNTHETIC RESINS

- cellulose/cellulose acetate
- synthetic alkyd
- chlorinated/cyclo-rubber
- vinyl
- acrylic
- polystyrene
- polyethylene

PH VALUE

13

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ BINDERS - SYNTHETIC RESINS (cont).

- styrene butadiene
- synthetic latex
- vinyl toluene
- phenolics
- epoxies
- urethanes
- polyamides (nylon)

PH VALUE

14

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ SOLVENTS

- dissolving binder
- viscosity adjustment
- plasticizers
- differing evaporation rates

#### ■ THINNERS

- viscosity adjustment mainly

PH VALUE

15

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ SOLVENTS

- aliphatics
- aromatics
- oxygenated
- alcohols
- chlorinated

pH VALUE

16

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## PAINTS AND COATINGS

### SOLVENTS

ALIPHATICS:	White spirit	Alkyds, acrylics
AROMATICS:	Toluene, xylene	Chlorinated rubbers, vinyls
ALCOHOLS:	Ethyl alcohol Butanols	Zinc ethyl silicate Epoxies
KETONES:	MEK	Epoxies
ACETATES:	Ethyl acetate, butyl acetate	Epoxies, polyurethanes

pH VALUE

17

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ WATER

- Water is usually not a solvent but a dispersing medium
- Water is reasonably fast evaporating and has good wetting properties
- Water vapour must be removed

pH VALUE

18

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ PIGMENTS

- organic or inorganic
- natural or synthetic
- prime pigments or extenders

PH VALUE

19

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ PIGMENTS AND EXTENDERS

- give colour and opacity
- regulates gloss
- mechanical strength
- UV protection
- corrosion inhibition or protection
- give chemical inertness
- give 'body' to the paint

PH VALUE

20

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## PAINTS AND COATINGS

### ■ FORMULATION

#### ■ PIGMENTS

- titanium dioxide
- zinc
- red/white lead
- brilliant leafing aluminium
- micaceous iron oxide (mica)

PH VALUE

21

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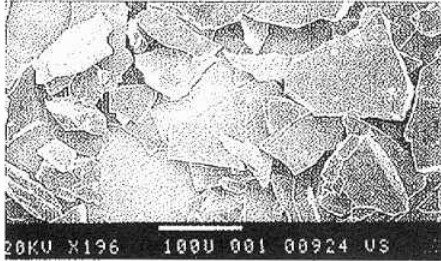
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## PAINTS AND COATINGS



**Mica**

pH VALUE

22

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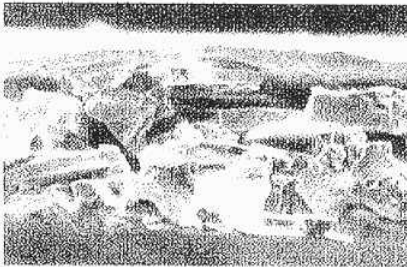
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## PAINTS AND COATINGS



**Mica (packing in film)**

pH VALUE

23

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## PAINTS AND COATINGS

- FORMULATION
  - PIGMENTS (cont.)
    - cuprous oxide
    - tri butyl tin
    - biocides
    - colour pigments
    - talc (extender)

pH VALUE

24

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## PAINTS AND COATINGS

### ■ PIGMENTS

### ■ COLOURING (Light reflection)



pH VALUE

25

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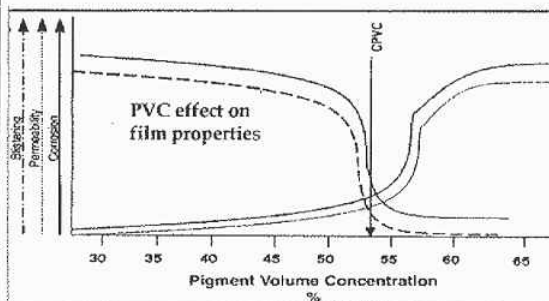
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## PAINTS AND COATINGS



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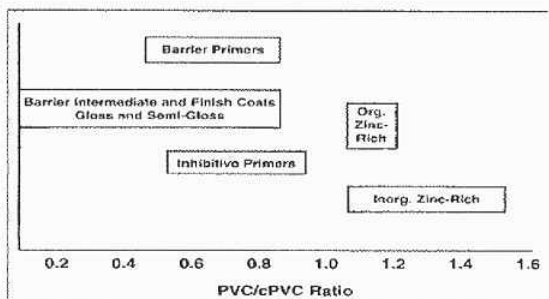
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## PAINTS AND COATINGS



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## PAINTS AND COATINGS

### ■ FORMULATION

- Drying additives
  - siccatives (manganese/cobalt salts with acids)
- Thixotropic additives
- Miscellaneous additives
  - anti-skinning
  - anti-gassing
  - biocides

gri VALUE

25

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## PAINTS AND COATINGS

### ■ FUNCTIONAL PRINCIPLES:

#### ■ BARRIER

- All paints work on this principle
- Use of special pigments like e.g. brilliant leafing aluminium, micaceous iron oxide to enhance barrier effect
- Alkyds - acrylics - epoxies - polyurethanes - silicones - vinyls etc.

gri VALUE

26

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## PAINTS AND COATINGS

### ■ FUNCTIONAL PRINCIPLES:

#### ■ INHIBITOR

- Inhibiting pigments like e.g. zinc phosphate, lead oxide, chromates (the last two taken out of formulations due to health considerations)
- Inhibiting effect is marginal
- Mainly used in industrial lacquers

gri VALUE

30

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## PAINTS AND COATINGS

### ■ FUNCTIONAL PRINCIPLES:

#### ■ GALVANIC

- Pigmentation in direct metallic contact with the steel substrate
- Pigmentation is mainly zinc powder
- Normally >85wt.% zinc in the cured film
- Best example is zinc silicate

pH VALUE

31

## PAINTS AND COATINGS

### ■ TYPES

#### ■ INORGANICS

- zinc alkali silicate
- zinc ethyl (alkyl) silicate
- cement based

pH VALUE

32

## PAINTS AND COATINGS

### ZINC SILICATES:

BINDER TYPE:	Alkali (e.g. Sodium potassium, lithium) silicate	Alkyl (e.g. Ethyl) silicate
DRYING:	Evaporation of water	Evaporation of solvent
CURING:	Reaction between zinc and silicate and also reaction between silicate, water and CO <sub>2</sub> in air	Reaction between silicate and humidity in air

pH VALUE

33

## PAINTS AND COATINGS

### ZINC SILICATES

#### ADVANTAGES

Chemically curing  
Quick drying  
Excellent adhesion  
Excellent chemical  
resistance  
Excellent weather  
resistance  
Extreme service life

#### DISADVANTAGES

Min. Sa 2½  
RH dependent  
curing  
Two-pack (multi-  
pack)  
Min curing times  
Air in pores  
(popping)  
High initial cost

pH VALUE

34

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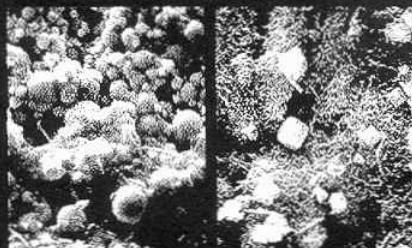
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## PAINTS AND COATINGS

### Zinc silicate



Unexposed, virgin coating      Seawater exposed coating

pH VALUE

35

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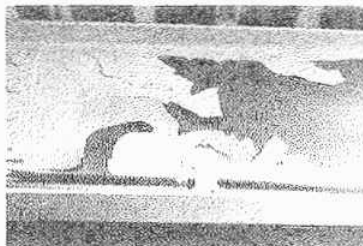
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## PAINTS AND COATINGS

Overcoating  
zinc silicate  
paint with  
alkyds is not  
a good idea



pH VALUE

36

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ CEMENT BASED

- ballast tanks
- potable water tanks
- alkaline
- often formulated with PVA

pH VALUE

37

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ PREFABRICATION PRIMERS (SHOP PRIMERS)

- alkyd
- PVB (polyvinylbutyral)
- epoxy
- zinc silicate (low and high  
Zn-content)

pH VALUE

38

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ WASH PRIMER (ETCH PRIMER)

- contains phosphoric acid!
- Extremely difficult to keep DFT down

BE VERY CAREFUL NOT TO EXCEED MAX  
DFT!

pH VALUE

39

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ ALKYDS

- short oil (chain)
  - hard, high gloss, fast drying
- medium oil (chain)
  - medium hard, gloss, drying
- long oil (chain)
  - soft, flexible, medium gloss, slow drying

pH VALUE

40

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## PAINTS AND COATINGS

### ALKYDS

#### ADVANTAGES

Oxidising  
Easy application  
One-pack  
Good wetting  
Good weather resistance  
Low cost  
Fair acid resistance

#### DISADVANTAGES

Poor alkali resistance  
Moderate water resistance  
Poor solvent resistance  
Recoating with other types is difficult (lifting)

pH VALUE

41

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ CHLORINATED RUBBER

- short supply
- specialised use only
- chlorine (HCl) problem

pH VALUE

42

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## PAINTS AND COATINGS

### CHLORINATED RUBBER

#### ADVANTAGES

Physically drying  
Easy application  
One-pack  
Good wetting  
Good weather resistance

#### DISADVANTAGES

Poor solvent resistance  
Low solids content  
Multi coat systems  
Thermoplastic

pH VALUE

43

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ VINYL

- supply = OK
- thin films (usually)
- chlorine (HCl) problem
- high cost per micr per m<sup>2</sup>

pH VALUE

44

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## PAINTS AND COATINGS

### VINYL

#### ADVANTAGES

Physically drying  
Good chemical resistance  
Good weather resistance  
Low water permeability  
Good flexibility

#### DISADVANTAGES

Low solids content  
Low solvent resistance  
Multi-coat systems  
High cost

pH VALUE

45

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ VINYL

##### ■ Vinyl tar

- good barrier (selected products only)
- mechanically weak

pH VALUE

46

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## PAINTS AND COATINGS

### VINYL TAR

#### ADVANTAGES

Low water permeability  
Moderate wetting  
Quick drying

#### DISADVANTAGES

Bleeding of tar  
Mechanically weak

pH VALUE

47

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ ACRYLIC

- replaces chlorinated rubber/vinyl
- thin films (usually)
- very versatile

pH VALUE

48

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## PAINTS AND COATINGS

### ACRYLICS

#### ADVANTAGES

Physically drying  
Easy to apply  
One-pack  
Good wetting ability  
Good weather resistance  
Low cost  
Reasonable acid resistance  
Redissolvable

#### DISADVANTAGES

Poor water resistance  
Poor solvent resistance

pH VALUE

49

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ SILICONES

- heat resistant
- thin films
- heat indicating
- Low surface contact antifoulings

- SILICONES ARE BOTH PHYSICALLY DRYING AND CHEMICALLY CURING (>200°C)

pH VALUE

50

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ BITUMENOUS/TARS

- brown/black only
- carcinogenic agents
- UV sensitive

pH VALUE

51

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ EPOXY

- polyamides
- polyamines
- amine adducts
- iso-cyanates

pH VALUE

52

## PAINTS AND COATINGS

### ■ TYPES

#### ■ EPOXY

curing agents are:

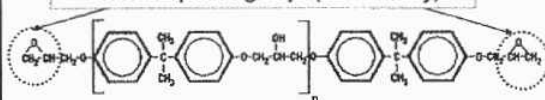
- amines
- amides
- adducts of the above
- ketamines
- ammonia based

pH VALUE

53

## PAINTS AND COATINGS

Reactive epoxide groups (functionality)



Where "n" is typically 1.0-1.3

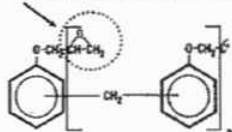
☐ Idealised structure of bisphenol A epoxy resin

pH VALUE

54

## PAINTS AND COATINGS

Reactive epoxide groups (functionality)



Where "n" is typically 1.5-2.2

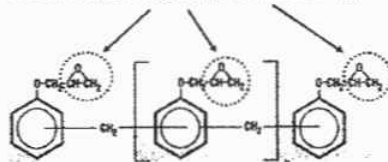
Idealised structure of bisphenol F epoxy resin

pH VALUE

55

## PAINTS AND COATINGS

Reactive epoxide groups (functionality)



Where "n" is typically 2.1-3.8

Idealised structure of epoxy novolac resin

pH VALUE

56

## PAINTS AND COATINGS

### ■ TYPES

#### ■ EPOXY

- Under very cold and damp conditions certain amines may separate out or be released from the film forming an 'oily' deposit on the film surface.
- This 'oily' deposit will destroy the intercoat adhesion and is popularly called 'amine sweating'.

pH VALUE

57

## PAINTS AND COATINGS

### ■ TYPES

#### ■ EPOXY

- solvent free
- solvent borne
- water borne
  - (solvent less?)

pH VALUE

58

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ EPOXY NICKNAMES:

- epoxy mastics
- epoxy phenolics
- normal temperature curing
- low temperature curing

pH VALUE

59

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## PAINTS AND COATINGS

### EPOXY

#### ADVANTAGES

Chemically curing  
Low water permeability  
Very good chemical resistance  
Very good adhesion  
High mech. strength

#### DISADVANTAGES

Temp. dependant curing  
Two-pack (multi-pack)  
High surface prep.  
Min/max times  
Recoating difficult

pH VALUE

60

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## PAINTS AND COATINGS

### ZINC EPOXY

#### ADVANTAGES

Chemically curing  
Quick drying  
Excellent adhesion  
High mech. Strength  
>85% Zn in dry film

#### DISADVANTAGES

Temp. dependant curing  
Low DFTs only  
Two-pack (multi-pack)  
Max/min times  
Poor acid/alkali  
resistance

pH VALUE

61

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ EPOXY

##### ■ Coal Tar Epoxy

- extremely good barrier
- contains PAH (polyaromatic hydrocarbons) - carcinogenic
- black/dark brown colour only
- bleeding

pH VALUE

62

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ POLYURETHANE

- solvent free
- solvent borne
- water borne
  - (solvent less)

pH VALUE

63

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ POLYURETHANE

- aliphatic polyurethane
- aromatic polyurethane

The aromatic type has the  
greatest health hazard

gpt VALUE

64

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ POLYURETHANE NICKNAMES:

- polyurethane mastic
- normal temperature curing
- low temperature curing

gpt VALUE

65

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ POLYURETHANE

- Polyurethane tar
  - extremely good barrier
  - contains PAH - carcinogenic
  - contains isocyanate

gpt VALUE

66

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## PAINTS AND COATINGS

### POLYURETHANES

#### ADVANTAGES

Chemically curing  
Quick drying  
Excellent adhesion  
Excellent chemical  
resistance  
Excellent weather  
resistance

#### DISADVANTAGES

Low temp. curing  
Recoating very difficult  
Two-pack (multi-pack)  
Max/min times  
Toxicity

pH VALUE

57

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ POLYESTER

- aliphatic polyesters
- aromatic polyesters
- abrasion resistant coatings

#### ■ VINYL ESTER

- hot water resistance

pH VALUE

58

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ TEMPORARY PROTECTIVE COATINGS

- Oil based
- Asphalt/bitumen based
- Wax based

Used for protection of machinery,  
parts etc. during storage and  
transport

pH VALUE

59

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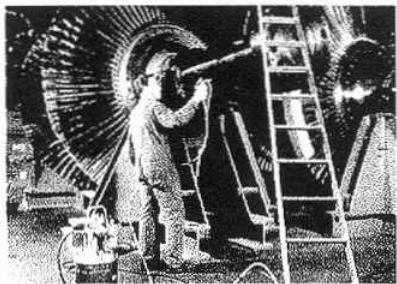
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## PAINTS AND COATINGS



Application of temporary protective coating

pH VALUE

70

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ WATER BORNE

- alkyds
- acrylics
- latex (PVA)
- epoxies (polyurethanes)

pH VALUE

71

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## PAINTS AND COATINGS

### ■ TYPES

#### ■ WATER BORNE

- Drying of water borne paints involve evaporation of water
- The binder is dispersed as minute globules in the water and through the evaporation the globules are brought into contact for film formation and curing (coalescence)
- Although the dry paint is insoluble in water, it is water sensitive during drying

pH VALUE

72

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## PAINTS AND COATINGS

### FORMULATION

Paint formulation is similar to most mixing processes where solid and liquid components are mixed, however, in some paint formulations there are also some chemical reactions involved, either reactions involved in the curing process or reactions among components

Paints and coatings are formulated using a large number of raw materials and additives, however, as basis for all formulations there are three basic groups of raw materials which form the basis for all paints and coatings. These basic raw materials are:

- Binders
- Pigments
- Solvents (or diluents or dispersants)

Below the three above generic groups of raw materials are discussed, followed by a discussion of other groups of raw materials and additives, as to their functions in the formulations and the properties they give to the dry film.

#### Binders

The binder or combination of binders is the vehicle binding the other components of the paint together during and after film formation. Binders also determine the film's adhesion to the substrate. Finally the binders are determining the properties of the dry film.

Most binders are organic in origin and may - at least as concerns the synthetic binders - be compared to plastics. There are three classes of binders, namely **natural**, **synthetic** and **inorganic** binders.

Binders or **resins** are natural or synthetic compounds that can form thin, continuous films, enabling them to be moulded into solid objects or spun into thread. They have broad, diverse chemical composition and many applications. Many resins are thick, viscous fluids, and others are hard, brittle, noncrystalline solids. Their molecular

structures may be complex, or they may consist of many relatively simple repeating units called monomers, which when combined, form polymers. Few resins are directly soluble in water, accounting for their use in areas where water resistance is paramount. Hydrocarbon solvents can make the vast majority of resins soluble.

The binder determines the drying and curing process of the paint. We distinguish between the following three main types of drying and curing as concerns paint:

- **physically drying**

These paints dry through the evaporation of solvents. Normally these types of paints redissolve when exposed to the solvents originally used in the formulation.

Examples of binders used in physically drying paints are: acrylics, chlorinated rubbers, cyclo-rubbers, vinyls, cellulose lacquers and most of the paints which are dispersed like, e.g. latex paint.

- **oxidatively curing**

These paints, besides solvent evaporation, also react chemically with the oxygen in the air. This reaction with oxygen is continuous and practically never stops.

A typical example of an oxidating paint is one based on alkyd as the binder. Oil-based paints also oxidize.

- **chemically curing**

Many paints we are designated as being chemically curing. The drying/curing process first implies that the applied wet film becomes partly dry through the evaporation of solvents. During this drying process, in which the wet paint film shrinks, the reactive components which commonly are called **base** and **hardener** (or **curing agent**) come into contact and will react with each other thus causing curing of the paint. The solvents will continue to evaporate also during this chemical reaction. Formulating chemically curing paints which do not contain solvents (or very little solvents) is also possible. Such paints are called **solvent free** (or **solvent less**).

Several binders are what we call **polymers**. Such polymers consist of long chains of molecular units. If these units are composed of only one type of molecules, we designate them **homo-polymers**, whereas polymers composed of two or more molecules are designated **copolymers**. A homo-polymer is thus a polymer composed of identical subunits (monomers of one kind); it is thus opposed to a copolymer, which contains more than one kind of subunit (monomers of various kinds). Many organic

substances that can be fabricated into films or fibres, such as polyethylene, nylon-6, and polyvinyl chloride, are homo-polymers. If chains of one homo-polymer are chemically joined to chains of another, the product is called a block or graft polymer.

Polymers are of two types: addition (repeated homo-addition of an unsaturated monomer to a growing chain) and condensation (loss of a small volatile molecule, usually water), between reactive ends of two poly-functional molecules. Polymers of the first type are often given names in which the prefix poly precedes the name of the source molecule. Polyethylene is such an addition polymer. Names for polymers of the second type also use the prefix poly, and must consider both poly-functional reactants in their polymerized form. The formal name for Dacron, for example, is polyethylene terephthalate. Polyurethane is another example.

A vinyl-acrylic copolymer is composed from alternating vinyl chloride and acrylic molecular units.

Polymeric compounds consisting of very long, two dimensional, molecular chains, are usually **thermoplastic**, e.g. they soften when the temperature increases. Polymeric compounds consisting of large molecules building a tridimensional grid are also called **reactive polymers**. Such polymers, of which epoxy and polyurethane are typical examples, do not soften through increases in temperature. Reactive polymers are not dissolved when they are exposed to the solvents originally used in the formulation of the paint.

### Natural resins

As the name infers, these are binders which are found in nature and used either as they are or with a certain amount of processing. In the origin of painting by the human race some very simple binders were used, e.g. the white of eggs and clays. Until and during World War II natural binders were extensively used, but have today been replaced by synthetic binders.

Natural binders include the following:

- asphalt
- pitch
- tars
- animal oils
- vegetable oils
- rosins

Asphalt, tars and pitch are used more or less as they are and mixed with whatever other components which the formulator deems necessary.

Animal oils include the following:

- **Fish oil** is not very much used today as there are other oils which are superior for production of alkyd resins, however, in the past fish oil was widely used, as was **whale oil**.
- Another natural resin of some past importance is **lac** (as used in SHELLAC). This clear, yellow or orange resin is secreted from the scales of an insect encouraged to colonize trees in sections of India and Thailand.

Vegetable oils include the following:

- **Soybean oil**, the world's largest-volume oil product, is a food. Much of the oil, which constitutes about 16% to 18% of the bean's weight, is modified before use. Soybean oil, often a constituent of paints and printing inks, is basic to the preparation of resins and plastics.
- **Linseed oil**, derived from flaxseeds grown mainly in Canada, Argentina, and the United States, is a drying oil because of the large amount of unsaturation present. Drying oils are used in protective coatings such as paints and varnishes. Linseed oil is also used in making linoleum and alkyd resins.
- The name resin once referred only to naturally available compounds, for example, rosin, capal, dammar, amber, and mastic. Today we distinguish these natural resins by designating them all as **rosins**. These are derived from vegetable sources and are collected as exudates from living trees and plants or extracted from stumps and heartwood of forested or fossilized trees. In most non-arid regions of the world, trees are cultivated or cut for their resin content. Resins from specific trees or localized sources, however, are often preferred. Dammar resin, for example, is derived from pines of the genus *Agathis*, native to Southeast Asia. It has been long favoured as a hardener for high-quality varnishes.

Common to all the above oils is that they are treated with various chemicals and heat to manufacture the alkyd resins. This process is popularly called **alkyd cooking**.

### Synthetic resins

In the 20th century the chemical industry experienced a dramatic growth in both technology and volumes produced. Increases in world population, the success of the automobile, and insatiable demands helped spur widespread research to develop synthetic products as replacements of inadequate resources. In addition, the quality and performance requirements of newly produced goods overtaxed the abilities of

existing resins.

- **Cellulose**, nitrated heavily during World War I to produce smokeless gunpowder, was modified to provide a film-forming resin. Although highly flammable, it offered exceptional qualities, such as high gloss, durability, and fast drying in inks, paints, and wood coatings.
- **Cellulose acetate**, another modification, was the basis for the fibre rayon but also used in certain lacquers.
- **Synthetic alkyd** resins, the backbone of modern solvent-borne paints and other varied products, were widely commercialized. These versatile resins essentially replaced the natural resin component in a varnish with esters of polycarboxylic acids and polyhydroxyl alcohols of excellent toughness and clarity.
- Demands for synthetic rubber during World War II led to the development of **styrene butadiene resins** and **latexes**. Some of these synthetic rubbers were treated with chlorine, resulting in **chlorinated rubber**, with **cyclic rubbers** as an alternative.
- **Vinyl** and **acrylic** resins, originally largely limited to military use, were later made available for general use. These resins offered unsurpassed stability and durability under the most adverse climatic conditions and eventually to a large extent supplanted other grades as paint binders and in exterior plastic displays, automobile coatings, and food packaging applications.
- Numerous other chemical varieties have proliferated in recent years. Such resins as **polystyrene**, **vinyl toluene**, **phenolics**, **epoxies**, **urethanes**, **polyethylene**, and **polyamides (nylon)** are available. They all offer specific qualities as films, plastics, or coatings.

Gloss is derived from the paint binder. To maintain maximum gloss, addition of pigment must be limited to relatively low volumes. Any fine-sized pigment may be employed, at concentrations not exceeding 20% by volume of the binder (excluding solvent or water). Increased pigment concentrations create a crowding effect within the dried film by which the pigment particles alter the profile of the surface, creating a reduction in reflected gloss. Eggshell and semigloss paints are available which exhibit little reduction in resistance properties due to preservation of a continuous film. Further addition of pigment produces additional crowding in the dried film and gradually overwhelms the ability of the film to encapsulate the pigment totally. Dry pigment particles protrude above the surface, producing a flat finish. This effect is particularly exaggerated if coarse particles are present.



The tiny cracks and crevices formed by the protruding particles in flat paints permit stains and other surface contaminants to become deeply embedded in the film and, therefore, difficult to remove. An added deficiency of such systems is the tendency for the exposed pigment particles to be loosely bound and, therefore, to be easily removed by mild abrasion. This produces burnishing, whereby a glossy or polished area is created in an otherwise flat background.

## Pigments

Pigments are a group of finely pulverized or processed, usually crystalline chemicals employed to colour and opacify materials and to protect or regulate product performance, quality, and appearance. Pigments, which are dispersed as solids, differ from dyes, which are used in solubilized form. Pigments may be organic or inorganic chemicals, and many are available directly from natural sources. They are classified as either **prime pigments** or **extenders**.

Prime pigments are used to impart colour or opacity or to perform specific functions. Their colour is a result of selective absorption and reflectance of visible light. Black pigments totally absorb light, whereas white pigments reflect all wavelengths. Colours have degrees of purity that depend upon whether broad or narrow portions of the visible spectrum are reflected.

Hiding, or the absence of transparency, is dependent upon differences in the refractive indices between prime pigments and the vehicle. **Titanium dioxide** is valued as an inert, white pigment with a high refractive index (2.76). Total hiding occurs when all incident light is refracted or diverted prior to completely penetrating a given film or object. Pigments for coatings and inks are highly valued for their ability to mask or hide surfaces in relatively thin films.

Prime pigments are often used for purposes other than colour or opacity. These pigments are mainly reactive types that chemically interact with binder components to toughen, thicken, or improve resistance properties. Others are employed to actively inhibit oxidation of ferrous metals or prevent growth of mildew, fungus, or barnacles.

The foremost active corrosion inhibitive pigment used today is **zinc**. Usually the pure **metallic zinc** is used. In former days lead oxides (**white and red lead**) were used, however, due to these compounds' toxicity they are in very little use today, and white lead is more or less forbidden to use in paints in most countries.

Pigments for the inhibition of growth of marine life are mainly **cuprous oxide** and **organic tin compounds**. The latter is the main biocide in the so-called self-polishing anti-fouling paints, however, cuprous oxide is also used in these and other types of anti-fouling paints.

A pigment commonly used for decreasing the permeability of paints is **mica**, also called **micaceous iron oxide**.

Extenders, also called **inert pigments** or **fillers**, are almost exclusively inorganic salts or oxides obtained directly from natural deposits. Processing is limited to refining and control of particle size. Inert pigments are added in relatively larger quantities than prime pigments to provide bulk volume, to thicken and fortify amorphous binders, and to influence such properties as gloss, hardness, and permeability. Though they are white when in powder form, their contribution to hiding and colour is negligible when applied because they are totally encapsulated in the binding media.

A typical extender is **talc**.

### Solvents

A solvent is a liquid chemical compound used for dissolving other compounds. Solvents are also used for the extraction of materials from other media, for the purification of solid substances by recrystallization, or as media in which to conduct chemical reactions. Water is one of the most important of all solvents, because it can dissolve many inorganic compounds and some organic substances, however, for the majority of the components going into a paint formulation water cannot dissolve these. In paint formulation, water usually acts as a **dispersant**.

A solution is a homogeneous mixture of one or several substances (the **solute**) in one or more differing, liquid substances (the **solvents**). From this we see that a solvent is a substance which is capable of dissolving the binder, and that the binder in paint formulations becomes the solute.

The principal qualification a liquid must possess to function as a good solvent is that it can dissolve another substance without reacting with it. A second important characteristic of a solvent is its volatility, as judged by its boiling point. Distillation or evaporation can remove solvents that have reasonably low boiling points readily from a reaction mixture or a recrystallization operation. The recent development of aprotic solvents (polar solvents of moderately high dielectric constant) such as dimethyl sulfoxide, N,N-dimethylformamide, and hexamethylphosphoric triamide has made commercially available a range of high-boiling solvents to function as reaction media at elevated temperatures.

Solvents may be classified in accordance with their solvency (dissolving power) and function relative to the binder component, as follows:

- **True solvents** have as their main function, the dissolution of the binder.
- **Latent solvents** can, when used in combination with true solvents, assist in

regulating the solvent evaporation rate and in the improvement of film properties (the latter mainly at elevated temperatures).

- **Diluents** can, when used in correct proportion with true solvents, also dissolve the binder, but are mainly used to improve the application properties and the film formation of the paint, as well as regulators for the evaporation of the solvent mixture in the paint formulation.
- **Reactive solvents** which take part in the curing process (mainly in chemically curing paints) either as a component in the process or as a catalyst.
- **Plasticizers** which have as a function to remain in the paint film after drying/curing to give flexibility to the film.
- **Thinners** are single solvents or solvent mixes which mainly have as function to adjust the application properties of the paint (mainly the viscosity). They can also have side functions such as assisting the film formation, regulating the evaporation rate of the solvent/thinner mixture.

The solvents used in paints are mainly derivatives from the petroleum industry and include the following generic groups and individual substances:

Aliphatics:	white spirit, SBP naphtha, hexane, heptane, high/low flash white spirits, odourless white spirit, turpentine etc.
Aromatics:	benzene, toluene, xylene, solvent naphtha etc.
Oxygenated:	acetone, methyl ethyl ketone (MEK), methyl iso-butyl ketone (MIBK), methyl iso-butyl carbinol (MIBC), ethyl acetate, butyl acetate etc.
Alcohols:	methanol, propanol, ethanol, butanol, benzyl alcohol, hexadecyl alcohol, ethylene glycol etc.
Chlorinated:	methylene chloride, trichloroethylene, perchlorethylene etc.

The solvency (ability to dissolve) is often giving as a Kauri Butanol value, and the above listing of groups of solvents reflects their increasing solvency ranging from the aliphatic solvents as the ones with the lowest degree of solvency, to the chlorinated solvents which have a very high solvency. However, not all of these solvents are used in paint formulations or as thinners.

## Driers

Driers are mainly used in oil and alkyd based paints. Oils or resins containing oils are converted when exposed to air by chemical oxidation and polymerization reactions. This process is accelerated by heat and also by the addition of compounds of cobalt,



manganese, lead, and other metals called driers (or siccatives).

### Additives

Additives of various nature are used in paints for widely differing reasons. Function of additives in paints are:

- Biocides to preclude bacterial growth (mainly in water borne paints).
- Biocides to stop fungus and lichen/moss growth on painted surfaces (mainly in house paints).
- Anti-foaming agents (to avoid foaming in water borne paints during production).
- Thixotropic agents (to avoid sagging).
- Curing accelerators.
- Dispersion agents (assisting in dispersion of the paint components).
- Anti-settling agents (to avoid bottom sediments in the can during storage).
- Anti-oxidants (to avoid reaction with oxygen during storage).
- Anti-skin agents (to counteract skin formation in the can).
- Anti-popping agents (to avoid popping when over coating zinc silicate paints).

Using the above raw materials and additives a formulator may work out recipes for various types of paints like the ones described below:

### Types of paint

Normally types of paint are **designated by their (main) binder component**, however, some few paints are designated by other components or by their main function. Such a system for designation is called a **generic system** and paints are often classified as generic types.

### Zinc rich paints

There are two types of zinc rich paints - organic and inorganic - which refer to their binder. The zinc content of these paints is normally at such a level that direct metallic contact between the zinc particles and the steel substrate is achieved. The zinc will by this be able to provide cathodic protection to the steel. Zinc rich paints are used as primers on steel and may be overcoated by other paints or left by themselves (for certain purposes).

### Organics

The most common binders used are either epoxy or polyurethane, although both vinyl and chlorinated rubber have been used. Oil or alkyd based binders cannot be used as

these will react with the zinc, forming zinc soaps. Synthetic binders which are non-saponifiable must be used in conjunction with zinc pigments.

Both epoxy and polyurethane are good insulators and it is therefore of prime importance that the zinc pigmentation is at such a high level that direct metallic contact between the zinc and the steel is ensured.

### Inorganics

Inorganic zinc containing paints are normally based on silicates as binder (or **vehicle** as binders are usually designated in this connection). We have two types of silicate binders - **solvent borne** and **water borne** - or **ethyl (alkyl) silicate**, respectively **alkali silicate**. Both types are two-component paints where the zinc powder is mixed into the liquid vehicle in pre-measured proportions prior to use. Silicates are electrically conductive and thus full electric contact between the zinc particles and the steel is ensured. The pigmentation may by this be kept at a lower level than what is the case for organics.

Zinc ethyl silicate paints dry through evaporation of the solvents in the vehicle. When these solvents are almost gone, the paint, which is porous, will be penetrated by air. When this air has a sufficiently high content of water, the semi-dry vehicle will react with this moisture and cure. The vehicle usually is supplied pre-condensated, which will assist in the curing process. Zinc ethyl silicate paints will not cure in environments where the relative humidity in the air is less than 50%, unless all areas are hosed down with water (fresh or sea water) to ensure curing.

Alkali silicates have a differing curing process in as much as the vehicle is dispersed in water. Curing starts when most of the water has evaporated and the paint is dependant on air movement over the surface so the water vapour is removed. If not, there is a real danger of the stagnant air close to the surface will be saturated and cause condensation onto the freshly painted and not yet water insensitive alkali silicate paint. The paint could thus be destroyed by its own water.

Both zinc ethyl silicate and zinc alkali silicate paints are mainly used as primers, and they are almost unsurpassed in their corrosion protection properties. Both have excellent mechanical properties and resist mechanical damages to a great extent. Both silicates can be destroyed by either strong acids or strong alkalies, however, inside a range of pH-values 6 - 9 they are very effective and are not attacked by very many chemicals.

The curing mechanism of the zinc ethyl silicate is somewhat sensitive, especially at high film thicknesses, due to the need for the film to absorb water from the surrounding air. The zinc alkali silicate paints do have superior properties as concerns mechanical

strength and longevity, however, being water borne it is limited to a minimum of +3-5°C as concerns allowable temperature during application. Zinc ethyl silicate, on the other hand, will cure at temperatures down to -10°C (provided that moisture in the surrounding air is above the minimum level required).

Both primers may be overcoated, however, only by paints based on non-saponifiable binders. It should be noted that both paints - when cured - are very porous in nature and that most paints applied in thick films will suffer popping from the air in the pores escaping through the freshly applied paint film. popping may be avoided through the use of paints having anti-popping agents incorporated into their formulation, or through the use of a **mist coat**. The latter technique implies thinning down the paint to be applied over the zinc silicate primer by some 25-60% and apply a thin (25-50 µm dry film thickness) mist like coat which will penetrate into the pores and replace the air.

Both zinc silicate types are widely used as tank linings.

### **Prefabrication primers (formerly designated shop primers)**

Steel plates, profiles and other suitable objects made from steel (e.g. pipes) are passed through what we term a prefabrication priming plant (shop priming plant) where they, after the steel has been cleaned in the centrifugal blast machine (wheel abrader), receive a coat of a special primer in a very thin dry film thickness.

There are many generic types of prefabrication primers and we classify them according to their generic binder and anti-corrosive pigmentation.

The binders used are the following:

- |   |                                   |  |
|---|-----------------------------------|--|
| - | <b>alkyd</b>                      | Very rare these days of advanced technological development.                                |
| - | <b>PVB<br/>(polyvinylbutyral)</b> | This type is still supplied in large quantities in certain areas of the world.             |
| - | <b>epoxy</b>                      | Large quantities consumed still of the two types existing (iron oxide and zinc pigmented). |
| - | <b>zinc silicate</b>              | Two basic types are supplied, namely high and low zinc content types.                      |

The pigmentation used in prefabrication primers for anti-corrosion purposes are:

- iron oxide
- zinc

Of these pigments, zinc may be used in both organic and inorganic prefabrication primers, whereas iron oxide is only used in organic binders.

Through the above designations we can describe a prefabrication primer very accurately:

- an iron oxide epoxy prefabrication primer, or
- a low zinc silicate prefabrication primer

Both the binder and the pigmentation has influence on some vital aspects connected to treatment of steel which has been prefabrication primed, however, the greatest influence is wielded by the dry film thickness to which these special primers are applied.

- Steel cutting speed is affected by binder, pigment and dry film thickness in as much as the cutting is slowed down to a lesser or greater extent. Diminishing the dry film thickness is the most important factor as concerns maintaining as high a cutting speed as possible.

It should be noted that plasma cutting is not affected by any of the mentioned factors due to the very high temperatures involved.

- The quality of the welding work is affected by both the binder and the pigments, as well as the dry film thickness. The formulation of the prefabrication primers very important, however, so is the dry film thickness applied, only more so. A unsuitable formulation or excess dry film thickness will lead to pores in the welds.
- Too high dry film thicknesses will give rise to unacceptable quantities of fumes from the burning and welding processes, and these fumes are at best irritants, and toxic at worst.

### **Wash primers**

Wash primers are based on polyvinylbutyral as the binder with a curing agent consisting of a mix between an alcohol and phosphoric acid. The product is two component and the components are mixed together just before use.

Wash primers have been used extensively for the below purposes.

- As a primer on degreased aluminium. The acid part will etch the surface of the aluminium and thus enhance adhesion.

- As a primer on metallized surfaces including hot dip galvanizing. Again the primer works as a preparation for the subsequent coating system.

Substantial problems have been encountered when using wash primers due to the fact that the primer has to be applied at an extremely low dry film thickness (5 - 15  $\mu\text{m}$ ). In higher dry film thicknesses the film will contain residues of the phosphoric acid which will cause problems with adhesion, blister formation etc.

Generally there is a tendency to avoid the use of wash primers as much as possible these days.

### Alkyd paints

The alkyd resin is made through reacting an oil with an acid and an alcohol, commonly called "alkyd cooking". Schematically an alkyd is produced as follows:

PHATALIC ACID ANHYDRIDE	C O O K I N G	➡	ALKYD RESIN
GLYCEROL		➡	
LIN SEED OIL		➡	
CHINA WOOD OIL		➡	

Alkyds are grouped in accordance with the length of the oil chain involved in the resin, and the following three groups are used:

- short chain alkyds
- medium chain alkyds
- long chain alkyds

The medium chain length alkyd are the ones usually used in anti-corrosion paints, however, the other two chain length alkyds are also used, however, mainly for specialized purposes.

Alkyds saponify in contact with zinc and may thus not be pigmented with metallic zinc, nor be applied directly on top of zinc silicate paint. Alkyd were in older days commonly mixed with lead compounds (both red and white lead) and this combination was very effective in preventing corrosion. Due to the problems connected to the toxicity of lead compounds, alkyds containing lead are not made very much anymore.

Alkyds are probably the most widely used type of paint and may be successfully applied

under a very wide range of ambient conditions, and onto marginally prepared substrates. Alkyds have very good penetration into pores in the substrate, and do not contain strong solvents which will cause lifting of underlying coatings. Alkyds are one-component products and may be applied by almost any type of application tools or equipment. They are thus very suited for maintenance as well as new construction work.

Alkyds are often mixed with other generic types of binders to enhance certain properties and the most common binder used in this way are chlorinated rubber, vinyl, silicones and urethanes.

Alkyd paints are oxidatively curing.

### **Chlorinated rubber paints**

Chlorinated rubber paints were originally manufactured through reacting natural rubber latex with chlorine producing a whitish powder, however, today the natural rubber has mainly been replaced by synthetic rubber. Due to the restrictions presently in force as concerns use of chlorine production of chlorinated rubber is limited and the use of this as a binder for paints is restricted to special products like, e.g. primers for underwater use.

Strong solvents like aromatics, ketones and chlorinated solvents are needed to dissolve the binder, and when dry, chlorinated rubber paints are redissolved in the original solvents used. This is an advantage as concerns adhesion between coats, however, this property makes chlorinated rubber paints limited for use in, e.g. chemical industry and on tankers where the paint may be in contact with strong solvents. The resistance against other types of chemicals like, e.g. acids and alkalies is good.

The permeability of this type of paints is low and this makes the paints well suited for use under immersion or heavy condensation conditions. Pigmenting chlorinated rubber paints with leafing aluminium or micaceous iron oxide further decrease the permeability of the paint. The binder is commonly combined with other binders like alkyds, acrylics and tars to make modified chlorinated paints with special properties.

Chlorinated rubbers are thermoplastic and this means that when the paints are subjected to elevated temperatures like, e.g. on the deck of vessels sailing in tropical waters, the paint becomes soft and tacky.

At temperatures above 60°C, chlorine may be released and precautions must be taken when welding on steel coated with chlorinated rubber paints. In fires, large amounts of chlorine gas is released, and this, apart from the health hazard, is a great problem in as much as the chlorine will react with moisture, forming hydrochloric acid (HCl) and this



acid can cause great corrosion damages.

Chlorinated rubber paints need surfaces to be cleaned more carefully than what is the case for alkyds, and abrasive blasting to Sa 2½ is commonly specified. These paints are not well suited for application by brush or roller due to their redissolving properties, and spray application is the best method.

### **Vinyl paints**

Vinyl chloride is a gas produced by reacting ethylene or acetylene with hydrochloric acid. The reaction replaces one hydrogen atom in ethylene with a chlorine atom; this modification makes the material non-burning. Polymerization produces polyvinyl chloride.

The vinyls are closely related to the chlorinated rubbers and have very much the same properties and limitations as these. Both chlorinated rubbers and vinyls have very low solids volume content and are thus expensive per micron per m<sup>2</sup>.

As is the case for chlorinated rubbers, vinyls are slowly phasing out of use, however, with one major exception. This is the use of vinyl in combination with tar for underwater use on ships' bottoms where the so-called **vinyl tar** paints are used both as a complete anti-corrosive system by itself or as a tie coat between an anti-corrosive system based on coal tar epoxy and the anti-fouling system.

### **Acrylic paints**

The acrylics have to a great extent replaced both chlorinated rubber and vinyl paints for general use in both land-based and marine industry. The acrylics are one-component and have very good colour and gloss retention properties. They can also to some extent replace alkyds where the yellowing tendencies of the alkyds are not desirable, thus warranting the somewhat higher price of the acrylics.

Acrylics reacted with isocyanate as a curing agent form extremely glossy and colour fast films and have found wide use in coating of aeroplanes, trains, buses etc.

Application of acrylics may be by brush, roller and spray.

### **Silicone paints**

There are numerous types of silicone based paints as silicone are often combined with either alkyd or acrylic resins. The prime feature of silicone-based paints is their resistance to high temperatures. Pure silicones will resist temperatures up to 600°C and have excellent weathering properties retaining gloss and colour better than most

paint types. Silicone paints usually have to be heated above a certain temperature to initiate the temperature resisting properties. When heated in this manner, certain chemical changes take place in the silicone paint film bringing forth the excellent heat resistant properties of this generic group of paints, and we therefore designate silicone paints as being both physically drying and chemically curing paints..

Silicone-acrylics resist temperatures up to 250°C and are less costly than the pure silicone-based paints. Silicone-acrylics may also be pigmented with special pigments which change colour at defined temperatures.

### **Bituminous and tar paints**

Both types are physically drying, one component paints mainly used on areas which are to be immersed. These types of paints are normally not pigmented and are either dark brown or black in colour. This plus the fact that both paint types are sensitive to ultraviolet light, limits their use.

In addition both bitumens and tars have been proven to be **carcinogenic agents** (substances causing cancer).

The bituminous and the tar based paints have been extensively used in e.g. ballast tanks and have shown good performance, however, other generic types of paint are replacing the bituminous and the tar based paints for this purpose presently.

### **Cement based paints**

Cement based paints are usually two component in as much as the cement (or cement/latex mix) is mixed with water or a water/latex mix. The paint in liquid or freshly dried state is highly alkaline and protect steel through passivation.

Cement based paints have found their use in protecting steel in ballast and potable water tanks and as protection for rebars used in concrete constructions, however, this protection does not last for any prolonged period of time, and thus cementitious coatings are mainly used on vessels having a short lifetime left.

Leaving the physically drying and oxidizing paints, we then turn to the **chemically curing paints**.

These paints are mainly two component paints where the paint (also called the base or the A-component) is supplied together with the curing agent (also called the hardener or the B-component) in separate containers. The two components must be mixed before use and in most cases mechanical mixing is needed. This mix must take place in a defined ratio between the two components and normally the volumes as supplied



are premeasured to the correct ratio. If this is not the case, the mixing ratio is either marked on the containers and/or stated in the technical data sheets for the paint in question. Mixing ratios are given either in volume or in weight terms (or both) so care should be taken to get the mixing ratio right.

The curing process of most chemically curing paints is dependant on temperature, which means the higher the temperature the faster the reaction goes. Usually the chemical reaction produce heat, i.e. what we call an **exothermic reaction**, however, some curing process need heat from the outside (e.g. baking) and such a reaction is called **endothermic**. When mixed together the chemical reaction between the two components start and we only have a certain time period from the point of mixing to the point of the paint having cured to a point where it cannot be applied anymore. This time period is called a paint's **potlife**. Some paints need to sit for a while prior to use in order for the two components to start reacting and this defined period of time is called **induction time**.

Chemically curing paints form dry films which are mechanically strong, non-thermoplastic and little affected by strong solvents or chemicals. The majority of the chemically curing paints protect steel through the membrane principle. Due to the hard, mechanically strong film which are formed, intact coating must be mechanically abraded before over coating during maintenance.

### Epoxy paints

Epoxy paints form the largest group of paints within the class of chemically curing paints. Epoxy film are mechanically strong and impact resistant and have a very good resistance to a wide range of solvents and chemicals.

The paint itself consist of epoxy resins with different chain lengths and we designate this as low or high molecular epoxies. The curing agents used are many, however, the most common ones are:

- polyamines
- polyamides
- amineadducts
- isocyanates

The group of synthetic resins called epoxies produce some of the strongest adhesives in current use, as well as plastics and corrosion-resistant coatings. Epoxy coatings are thermosetting; that is, after initial hardening, they cannot be remelted by heat. They have excellent resistance to solvents and weathering agents, and high electrical and temperature resistance. Their adhesion to almost any type of surface - including metal, ceramic, wood, and fabric - is almost unmatched.

Epoxyes are usually made by reacting epichlorohydrin and Bisphenol A to produce a polymer chain of somewhat complex structure. The end of the polymer chain is an epoxy group from epichlorohydrin; the resulting plastic receives its name from the end epoxy group.

The unmodified epoxyes are brittle; however, the properties of the cured resin can be varied widely by the selection of a suitable resin, curing agent, filler, and curing procedure. Flexible grades are modified with polyamines and polysulphides. Most epoxy formulations have two components that are mixed for curing. One-component epoxyes are available that either contain a latent curing agent or are simply cured by absorption of oxygen from the air. One example of such one-component epoxyes are **epoxy-ester paints**. Unlike most thermosetting plastics, epoxyes shrink only slightly during curing. Epoxyes can be used as filler-adhesives; the strength of the cemented joint is independent of its thickness.

The epoxyes are used as moulding and potting compounds, reinforced plastics, surface finishes, and adhesives. Moulding compounds are chiefly used by the electronic and electrical industries; potting compounds are poured to encapsulate small electronic parts. Epoxy paints have outstanding corrosion resistance and are permitted for use on food equipment such as flour bins and can coatings.

Epoxy coatings may be subdivided into the below groups:

- solvent free
- solvent less
- solvent borne
- water borne

Both the solvent free and the solvent less (e.g. coatings with a very low content of solvents - <5-20 vol.% solvents) are based on low molecular epoxy resins. The solvent borne types are usually formulated from high molecular epoxy resins, which require very strong solvents. The water borne types may be based on both resin types.

The various curing agent used give differing properties to the epoxy paint film. Polyamides give dry films which are very little water permeable, however, the curing process is somewhat slow. Combinations of polyamines and amineadducts give films with increased resistance to solvent and chemicals and speeds up the curing process. Use of isocyanates as curing agents enables curing below 0°C, however, the health hazards to workers are increased.

Apart from alkyds, epoxy paints are the most widely used today for corrosion protection of steel and other metals. These paints have excellent resistance to solvents, chemicals and pollution and are used in, e.g. refineries, chemical plants, industrial

environments in general and on ships.

A special class of epoxies which have come to the forefront in later years are termed **epoxy mastics**. These are solvent less materials with lower demand as to surface cleanliness than epoxies (which usually need abrasive blasting to Sa 2½ standard). The original mastics were pigmented with aluminium, however, presently products pigmented either with micaceous iron oxide or normal colour pigments, are available. The latest development is mastics with low temperature (down to -10°C) curing properties.

One special class of epoxy materials are termed **coal tar epoxy** or **tar epoxy**. In these products part of the epoxy binder has been replaced by tar. Originally the replacement was coal tar (tar resulting from distillation of coal), however, due to the need for reducing the cost price of the paint, other tars and even bitumens are used in formulations. Also, formulations deviating from the original one of a 50:50 mix of epoxy and coal tar has been deviated from, increasing the tar/bitumen component and reducing the epoxy. However, the excellent properties of the original formulation of the coal tar epoxy will also be changed through major deviations, creating products with inferior properties as to water permeability. Major failures in e.g ballast tanks have been seen where the origin of the problem clearly can be traced to a too high content of bitumen in the paint's formulation.

Epoxy paints have a tendency to yellow and chalk when exposed to ultraviolet light and are not very effective as final or decorative coats for outdoors use.

Application of epoxy paints may be done by most tools and equipment, however, they lend themselves to spray application most readily. Apart from observing the potlife, minimum and maximum recoating intervals must be observed in multi-coat systems.

### **Polyurethane paints**

Polyurethane paints are very similar to epoxies both in nature and in use. The polyurethanes do not have the epoxies' weakness towards ultraviolet light and have excellent gloss and colour retention properties. However, due to the use of isocyanates as curing agents, the health aspects are more serious than what is the case for epoxies. The binder may be either aliphatic or aromatic in nature and whereas both types present health hazards, the aromatic types are the most perilous ones. In fires, cyanide gas may be released from the burning coating, and this gas is extremely toxic.

Isocyanates have a tendency to react more readily with water than with the polyurethane and this makes the paint vulnerable to condensation during the early stages of the curing process. In some formulations this "weakness" is explored in as much as water from the air is used to cure the coating. Such coatings are termed

**moisture curing.** Most of the moisture curing polyurethanes are one-component.

The following basic types of polyurethanes are manufactured:

- solvent free
- solvent less
- solvent borne
- water borne

Polyurethanes are often used in combination with epoxies in coating systems. Usually they are used as finishing coats due to their outstanding colour and gloss retention properties. Furthermore, the isocyanate curing agents enable polyurethanes to cure at temperatures ranging from 0°C down to -20°C.

As for the epoxies, **mastic types** of polyurethanes have emerged in later years, however, with the emergence of the amine adduct, low temperature curing epoxy mastics, the need for polyurethane mastics may not be present.

Like epoxies, polyurethanes may be combined with tar, however, due to price these polyurethane-tars are mainly used for special purposes like, e.g. pipe coating.

Application of polyurethanes

### **Polyester paints**

Polyesters are a class of long-chain polymers characterized by formation through ester groups. There are four major classes of polyesters, each with its specific composition and applications: alkyds, unsaturated polyesters, polyethylene terephthalates, and aromatic polycarbonates.

An example of a difunctional molecule is hydroxy acid. The hydroxyl (OH) group of one hydroxy acid monomer reacts with the carboxyl group (COOH) of another hydroxy acid monomer to form an ester (a dimer). The ester dimer is also difunctional and may react further to form a polyester, where *n* is the number of repeating units in the polymer chain. Polyesters may also be formed by reacting a dihydric alcohol (glycol) with a dicarboxylic acid.

In paint formulations unsaturated polyesters are used in combination with **styrene** as curing agent. The unsaturated polyesters are normally aliphatic in composition and thus present less health hazards to workers using this type of paints than the aromatic types based on e.g. aromatic polycarbonates.

Polyester paints are frequently formulated with pigmentation of glass flakes. This is to decrease the water permeability of the coating film and also increase the mechanical properties of the coating film.

A special version of this class of paints are **vinyl ester paints**. These have excellent resistance to water at high temperatures/steam, and are typically used in condensation tanks in refineries and chemical plants.

### **Water borne paints**

What we see and feel on a painted surface are the solid parts of the dried liquid paint, called binders and pigments. In the past, the binders were dissolved in organic solvents. In the waterborne paints the organic solvents are almost absent, and the binder, in form of small spheroids, is dispersed in water. In most cases, the binder is what we call an emulsion type.

An **emulsion** is a stable mixture of two or more immiscible liquids held in suspension by small additions of substances called emulsifiers.

A **dispersion** is a two-phase system where one phase consists of minute particles distributed through a bulk substance, and the other phase of minute spheroids of an emulsion distributed through the same bulk substance.

The binders commonly used in water borne formulations are:

- alkyds
- acrylics
- latex (PVA)
- epoxies
- polyurethanes

After application, the water evaporates and the binder spheroids through this comes in direct contact with each other and will coalesce - a process not unlike the coalescence of blood from a scratch.

It should be noted that the waterborne paints are not completely solvent free, as they do contain small amounts of special solvents called plasticisers, which are needed to ensure that the coalescence takes place. The solvent content is, however, kept at a very low level, usually well below 6%.

Apart from the mentioned reduction in solvent emissions, the waterborne paints offer the following advantages:



- A better and safer working environment. Operators working with these paints, as well as other people working in adjacent areas, have their exposure to the harmful solvents emitted, greatly reduced.
- Solvent vapours present fire and explosion hazards which are not present when using waterborne paints.
- Shipboard maintenance with waterborne paints do not introduce unpleasant smells throughout the ship, and hence maintenance on e.g. cruise liners and ferries may proceed without passengers being unduly disturbed.
- Waterborne paints have equal or superior properties as compared to the physically drying, solvent borne products.

Surprisingly, the waterborne paints do not give users many disadvantages, however, below are listed some:

- Application at temperatures below 5°C is not recommended.
- Good ventilation is needed during the drying period.

Users will of course look very carefully into the technical properties of the waterborne paints in order to determine if a switch to this type of materials will mean a reduction in quality from what they are using today.

Experience from a variety of applications all over the world during the last decade, shows that the waterborne paints provide protection against corrosion at least as good as that being provided by solvent containing alkyd, acrylic and chlorinated rubber paints.

This experience has been gained from large scale use of water borne products for corrosion protection of containers, non-immersed parts of ships, structural steel in industrial plants and offshore structures.

Water borne paints have a superior adhesion to all kinds of substrates, as compared to traditional paints. Such substrates include aluminium and galvanized or stainless steel. Furthermore, the well known problem of lifting of existing coats of paint from the solvents in subsequent coats, simply does not exist when using waterborne paints.

Water borne finish coatings both in outdoor exposure tests and in practice, show themselves to have a higher degree of both gloss and colour retention over time, than comparable, solvent borne finishes. Compared to e.g. the alkyd paints generally used aboard ships, the water borne finishes do not exhibit the same tendencies to yellowing. Furthermore, the water borne acrylic coatings have good resistance to lubricating oil, which make them ideal for use in a vessel's engine room.

Waterborne acrylic paints have a high degree of flexibility, which makes them very well suited for use aboard a ship.

In general, there are no significant differences in the methods and tools of application

when switching from solvent borne to waterborne paints. Both types of materials have a number of particulars and conditions which must be observed in order to ensure successful application of the product in question.

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