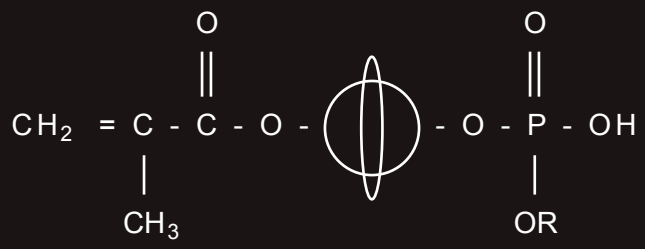
ADDAPT
Chemicals BV

for tomorrow's
Technology



PolySurF™

Functional Monomers
Radiation Curing Additives

for tomorrow's
World

Contents

1. Introduction

There is an increasing demand for the development and use of environmental friendlier raw materials and products due to legislation and, ever so important: customer demand.

The composition and use of solvent based products such as paint, adhesives and printing inks has already changed dramatically but need further changes in coming years. The demand for new, environmental friendlier systems is therefore stronger than ever, not only based on ecological reasons but also due to increasing quality demand.

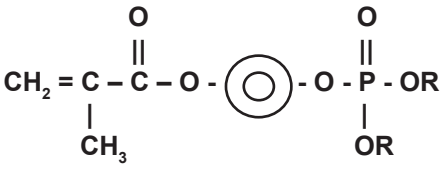
It has been shown that a solution for both problems is possible: new water based systems having low or no emission of volatile materials showing performance matching the classic solvent based systems. Main part of this success can be attributed to a new generation of additives allowing more formulation freedom.

ADDAPT Chemicals offers, amongst other, a new generation of functional monomers/additives for use in emulsion polymerisation or use as additives in UV/EB-curable systems.

This brochure gives an overview of the ADDAPT® PolySurF™ products for use as adhesion promoters, polymerisable stabilisers, polymerisable plasticiser and polymerisable wetting agents.

2. Properties

2.1 ADDAPT® PolySurF™ HP R=H




= Hydrophobic group

Av. Molecular Weight: 250

Suggested applications:

- Radiation Curable systems.
- Co-monomer in Poly Acrylic Pigment Dispersants.
- Polymerisable Stabiliser for Emulsion Polymerisation Processes.
- Suggested end-use:
  - Paints & Coatings (primers; wet-scrub improvement of emulsions etc.)
  - Adhesives & Bonding Agents
  - Pigment Dispersants
  - Printed Circuit Board (PCB) – Solder Masks & Etch resist film
  - Photographic Film
  - Detergents & Cleaners
  - Radiation Curable Metal primers and finishes
  - Superabsorbents

Product benefits:

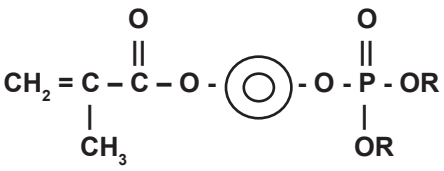
- Excellent Mechanical Stability – Non Migratory (Emulsion Polymerisation).
- Excellent Polyvalent cation tolerance (Ca^{2+} etc.).
- Improved properties over (Meth)acrylic acid in Emulsion Polymerisation.
- Highly reactive – good compatibility with Acrylic and Methacrylic esters.
- Excellent Adhesion Promoter to all metal substrates, metal-oxides, glass, ceramics and concrete.
- Imparts very good corrosion inhibiting properties after polymerisation.
- Gives flame retardant properties due to the Phosphor content.

Note: ADDAPT® PolySurF™ HP is not a surfactant and as such has no HLB-value.

Typical chemical and physical characteristics:

Appearance	Clear liquid
Odour	Sweet smell
Viscosity at 25 ºC	1250 - 3500 mPa.s
Colour	max. 4 Gardner
pH	0.5 to 3.0
Phosphorus content	ca. 12%
Active content	> 99.5%

2.1 ADDAPT® PolySurF™ HEOP R=H



= 3.5 > EO < 4.5

Suggested applications:

- Radiation Curable systems.
- Polymerisable Stabiliser for Emulsion Polymerisation Processes.
- Suggested end-use:
  - Paints & Coatings (primers; wet-scrub improvement of emulsions etc.)
  - Adhesives & Bonding Agents
  - Pigment Dispersants
  - Printed Circuit Board (PCB) – Solder Masks & Etch resist film
  - Photographic Film
  - Detergents & Cleaners
  - Radiation Curable Metal primers and finishes
  - Superabsorbents

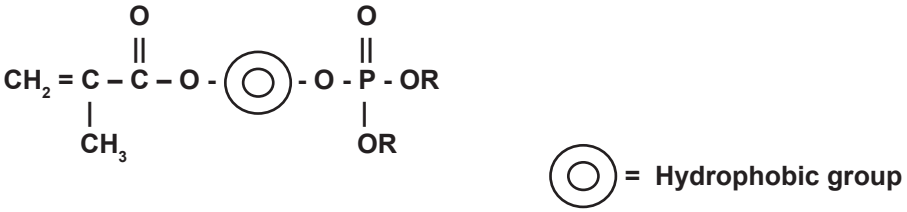
Product benefits:

- Excellent Mechanical Stability – Non Migratory (Emulsion Polymerisation).
- Excellent Polyvalent cation tolerance (Ca^{2+} etc.).
- Improved properties over (Meth)acrylic acid in Emulsion Polymerisation.
- Highly reactive – good compatibility with Acrylic and Methacrylic esters.
- Excellent Adhesion Promoter to all metal substrates, metal-oxides, ceramics and concrete.
- Imparts good corrosion inhibiting properties after polymerisation.
- Imparts freeze/thaw stability.

Typical chemical and physical characteristics:

Appearance	Clear liquid
Odour	Sweet smell
Viscosity at 25 ºC	< 2500 mPa.s
Colour	max. 4 Gardner
pH (1% solution)	1.6 to 2.0
Phosphorus content	10.5%
Active content	> 99.5%

2.3 ADDAPT® PolySurF™ HPH R = - $(CH_2\ CH_2O)_{10}$



Suggested applications:

- Radiation Curable systems.
- Co-monomer in Poly Acrylic Pigment Dispersants.
- Polymerisable Stabiliser for Emulsion Polymerisation Processes.
- Suggested end-use:
  - Paints & Coatings (Wood finishes; Metal coatings; Mirror Backing Films)
  - Adhesives & Bonding Agents
  - Pigment Dispersants
  - Printed Circuit Board (PCB) – Solder Masks & Etch resist film
  - Photographic Film
  - Detergents & Cleaners
  - Radiation Curable Metal primers and Wood finishes

Product benefits:

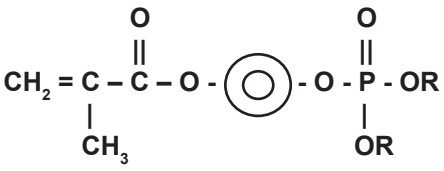
- Excellent Mechanical Stability – Non Migratory (Emulsion Polymerisation).
- Excellent Polyvalent cation tolerance (Ca^{2+} etc.).
- Improved properties over (Meth)acrylic acid in Emulsion Polymerisation.
- Highly reactive – good compatibility with Acrylic and Methacrylic esters.
- Very Good Adhesion Promoter to all metal substrates.
- Imparts very good corrosion inhibiting properties after polymerisation.
- Improves wetting on metal and wood substrates in Radiation Curable Systems.

*Note: ADDAPT® PolySurF™ HPH is not a surfactant and as such has no HLB-v*alue.

Typical chemical and physical characteristics:

Appearance	Clear liquid
Odour	Sweet smell
Viscosity at 25 ºC	< 350 mPa.s
Colour	max. 2 Gardner
pH	< 3.0
Phosphorus content	ca. 6.5%
Active content	> 99.5%

2.4 ADDAPT® PolySurF™ HPL R = - $(CH_2)_{10-12}$



= Hydrophobic group

Suggested applications:

- Radiation Curable systems
- Co-monomer in Poly Acrylic Pigment Dispersants
- Polymerisable Stabiliser for Emulsion Polymerisation Processes
- Suggested end-use:
  - Paints & Coatings
  - Adhesives & Bonding Agents
  - Printed Circuit Board (PCB) – Solder Masks & Etch resist film
  - Photographic Film
  - Radiation Curable Metal primers and finishes

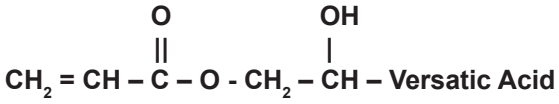
Product benefits:

- Excellent Non Migratory Plasticiser
- Highly reactive – good compatibility with Acrylic and Methacrylic esters
- Very good Adhesion Promoter to all metal substrates
- Very good Corrosion Inhibitor for Metal pastes (Bronze and Aluminium pastes)
- Imparts very good corrosion inhibiting properties after polymerisation.

Typical chemical and physical characteristics:

Appearance	Clear liquid
Odour	Sweet smell
Viscosity at 25 ºC	50 - 300 mPa.s
Colour	max. 2 Gardner
pH	0.5 to 2.0
Phosphorus content	ca. 10%
Active content	> 99.5%

2.5 ADDAPT® PolySurF™ ACE



Suggested applications:

- Radiation Curable systems.
- Co-monomer in Poly Acrylic Pigment Dispersants.
- Co-monomer for Emulsion Polymerisation Processes.
- Suggested end-use:
  - Paints & Coatings (Wood finishes, Automotive finishes)
  - Adhesives & Bonding Agents
  - Pigment Dispersants
  - Printed Circuit Board (PCB) – Solder Masks & Etch Resist film
  - Radiation Curable finishes

Product benefits:

- Polymerisable Monomer with excellent pigment wetting properties.
- ADDAPT® PolySurF™ ACE improves adhesion to Polyolefin's, Polyethylene Therephtalate and Polyvinylchloride.
- Imparts Hydrophobic properties in Emulsions.
- Highly reactive – good compatibility with VEOVA, Styrene, Acrylic,and Methacrylic esters.
- Good Acid resistance.
- Contains a reactive sec. OH-group for improved intercoat adhesion.
- Imparts good UV stability in resins after polymerisation.

Typical chemical and physical characteristics:

Appearance	Clear liquid
Odour	Acidic smell
Viscosity at 25 ºC	< 300 mPa.s
Colour	max. 2 Gardner
pH	2.5 to 4.5
Tg of homopolymer	0 °C
Active content	> 99.5%

3. Application

3.1 Emulsion Polymerisation

Natural latexes have been used for many centuries. In fact, synthetic rubber latexes, which were among the first commercial products of emulsion polymerisation processes, became important as a substitute for natural rubber.

Modern synthetic latexes find application as coatings, printing ink, (pressure sensitive) adhesives, binders in paper, paper coating and textile products, medical products and many other areas. These products are normally marketed and used in latex form. Other products such as elastomers and engineering plastics are separated from the aqueous phase prior to use.

Emulsion polymers are produced in a wide variety of processes. Conventional emulsion polymerisation involves the dispersion of an organic monomer in an aqueous phase with an oil-in-water emulsifier followed by polymerisation with a free-radical initiator that is normally water-soluble. The product is a colloidal dispersion of polymer particles called latex. The terms latex, polymer colloid and emulsion polymer are used synonymously in this article.

Ingredients for a typical emulsion polymerisation system include:

- Water – the continuous phase
- **Emulsifiers and Stabilisers**
- **Monomer or Monomer Mixture**
- Initiator system
- Minor ingredients – additives (Defoamer, Biocide etc.)

The choice of Emulsifiers, Stabilisers, monomers and combinations thereof, together with the initiator system will, to a large extend, determine the end-properties of the resulting polymer like: film formation, flexibility, water sensitivity etc.

3.1.1 Emulsifiers and Stabilisers

Emulsifiers (surfactants) and Stabilisers are used in emulsion polymerisation to optimise colloidal stability of the emulsion during polymerisation, storage and application including optimisation of the film formation process.

Traditional Surfactants increase water sensitivity of the final film due to surfactant migration (blooming) towards the film surface. **Polymeric Surfactants** were launched to establish an irreversible absorbed protective layer to the particle surface. Although slow, migration of these surfactants is however still likely to occur. Also in certain cases these polymeric surfactant have the tendency to re-emulsify and/or give rise to an undesirable continuous platicizing or softening effect.

In addition to Emulsifiers, **Stabilisers** like Acrylic acid, Methacrylic acid and Itaconic acid are used to further optimise the stability of the emulsion. Major drawbacks are increased water sensitivity, poor polyvalent cation stability and in case of Acrylic acid, homo-polymerisation leading to highly water sensitive polyacrylates oligomers.

3.1.2 PolySurF™ – advantages in Emulsion Polymerisation

The Hydrophobic moiety next to the Phosphonate in the PolySurF™ products prevents undesirable saponification as sometimes observed in Sulfonate containing alternatives.

As a polymerisable Stabiliser, the PolySurF™ HP achieves exceptional mechanical stability in emulsion coatings. It becomes an integral part of the film, resisting leaching. It improves adhesion to metal surfaces and gives anti-corrosion properties. It is an excellent alternative for Acrylic acid, improving the tolerance towards Ca^{2+}-ions.

PolySurF™ HPH functions as an ethoxylated non-ionic stabiliser recommendable for non-ionic stabilised emulsions. Next to being a very good adhesion promoter for metal surfaces, it also gives very good wetting of metal and wood surfaces when incorporated into the emulsion polymer.

Pressure Sensitive Adhesives for instance have been negatively affected by the move towards water based formulations. Poorer adhesion was attributed to the migration of surfactants in the emulsion causing failure between adhesive and substrate. Incorporation of PolySurF™ HPH could overcome such problems.

PolySurF™ HPL can be used as a polymerisable plasticiser via emulsion polymerisation. Becoming an integral part of the final polymer, no migration will occur. PolySurF™ HPL can also be recommended for production of PVC via emulsion polymerisation.

3.1.3 Corrosion Resistant Primer Emulsion

Description: VEOVA/Acrylate copolymer emulsion showing an excellent level of salt spray resistance when formulated in Corrosion Resistant Primers.

Number	Amount (Kg)	Raw material
Initial reactor charge		
No. 1	1000.0	Water demi
No. 2	200.0	ADDAPT® PEX™ 136 (See Note 1)
No. 3	7.0	ADDAPT® PolySurF™ HP
No. 4	10.0	Ammonium Hydroxide 25%
No. 5	2.0	Potassium Persulphate
No. 6	154.0	Water demi
Monomer pre-emulsion		
No. 7	1200.0	VEOVA 10
No. 8	600.0	MethylMethacrylate
No. 9	140.0	Butyl Acrylate (or 2-Ethylhexyl Acrylate)
No. 10	200.0	ADDAPT® PEX™ 136 (See Note 1)
No. 11	8.0	Potassium Persulphate
No. 12	14.0	ADDAPT® PolySurF™ HP
No. 13	20.0	Acrylic acid (See Note 2)
No. 14	953.0	Water Demi
No. 15	4.0	Proxel XL2 (or identical) ex-Zeneca
No. 16	21.4	Ammonium Hydroxide 25%

Note 1: ADDAPT® PEX™ 136, 10% aqueous solution, pH=9
Alkyl ethoxylate phosphate ester (ADDAPT Chemicals BV)
Note 2: Depending on stability and grit formation, if possible avoid usage and substitute by PolySurF™ HP.

Procedure

I. Charge (1) to the reactor and heat to 80 °C under a flow of nitrogen.
II. Dissolve (2), (3), (4) and (5) in water (6) and charge to the reactor. Meanwhile the reactor is purged with nitrogen.

III. When the temperature reaches 80 ºC again, the nitrogen flow is stopped.
IV. Mix (7), (8) and (9) and add under stirring (10), (11), (12), (13) and (14) until a stable pre-emulsion is obtained.
V. Add 2.5% (volume) of this pre-emulsion to the reactor (seed).
VI. After a period of five minutes, the remaining pre-emulsion is added to the reactor during 3 hours at 85 ºC.
VII. After dosage, keep the temperature at 85 °C for two hours.
VII. Cool down to T< 30 °C and add (15) and (16).

Properties

Solid content	45.0 ± 0.5%
MFFT	15 ºC
pH Emulsion	8.0 ± 0.5
Viscosity Emulsion	450 ± 75 mPa.s (Brookfield)

3.2 Radiation Curing

Adhesion to metals and plastic surfaces remain a challenging problem of formulators of UV/EB curable systems. In many cases, these substrates must be cleaned or pre-treated to remove residual dirt, oil or oxidation residues that exists on the surface.

Soiled surfaces will also give poor wetting of the surface thereby negatively influencing adhesion and give rise to surface defects of the final coating.

Formulations are therefore aimed to develop systems which not only wet the surface, but upon curing, exhibit low shrinkage to minimize stress and to optimise bond formation with the surface of the substrate. Although a proper choice of the oligomers system plays an important role, use of functional additives like PolySurF™-products can bring the final desired properties.

In paragraph 3.2.1 some typical formulations, using PolySurF™ products as additive, are shown.

3.2.1 Radiation Curable Metal and Plastic coatings

UV curable coating for Polycarbonate

Component	%
Tris (2-Hydroxyethyl) Isocyanurate Triacrylate (SR-368)[1]	35.0
1.6 Hexanediol Diacrylate	29.0
Pentaerythritol Tetraacrylate	29.0
ADDAPT® PolySurF™ HPL	2.0
Darocure 1173[2]	3.0
Irgacure 184[2]	2.0

[1] SARTOMER, [2] CIBA additives

UV curable clear coating for Aluminium

Component	%
Polyester Acrylate Oligomer, low Mw. (1000)[1]	26.0
ADDAPT® PolySurF™ HP	1.0
ADDAPT® PolySurF™ HPH	2.0
PHOTOMER® 4028[1]	10.0
PHOTOMER® 4039[1]	20.0
PHOTOMER® 4072[1]	33.0
PHOTOMER® 81[1]	3.0
Darocur 1173[2]	3.0
Triethanolamine[3]	2.0

[1] COGNIS - RCC 13-429, [2] CIBA additives, [3] BASF

Further formulations are available upon request.

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