







November 2021

WEBINAR IX



SAPPMA Webinar I to VII on SAPPMA Web site







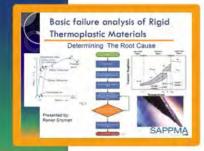


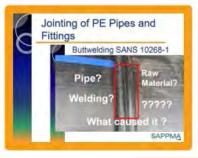






















Recent CPD training event















Thermoplastic Pipe Systems:

Important aspects to understand and keep in mind during design and specification















What is your formula to success?



Did you factor in the unknows?

Are you Rigid or Flexible?

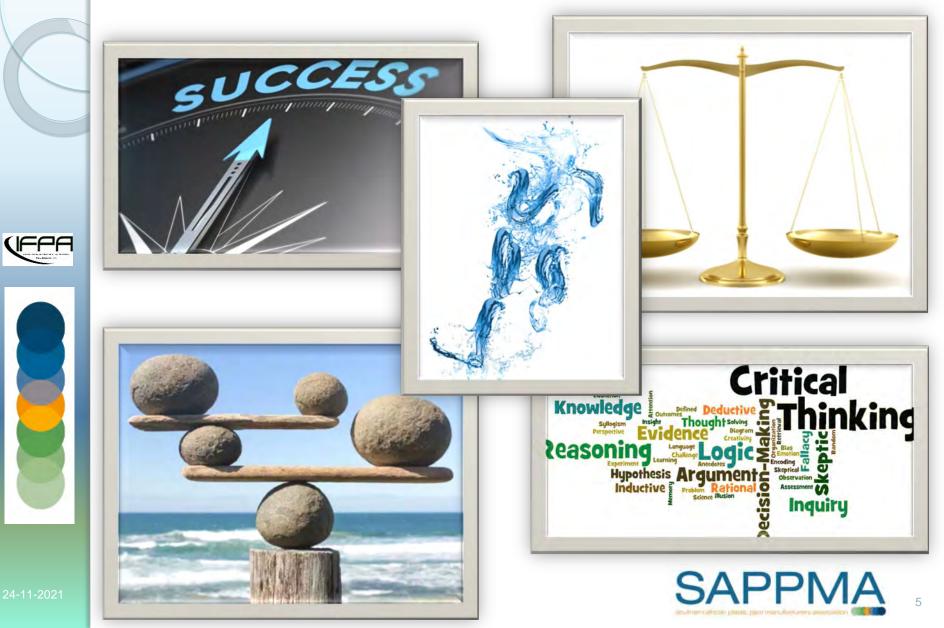
How does it compare to what we know?



Does it all add up?



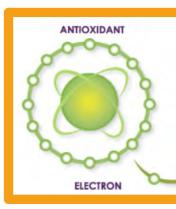
(Critical to Quality) CTQ & CTS (Critical to Success)







SAPPMA Webinar IX







SAPPMA invites you to its 9th Webinar for 2021

DATE: 24 Nov 2021

TIME: 9:00 to 10:30 (Registration from 8:45)

PLATFORM: ZOOM

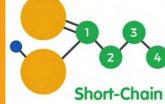
Gelation of Extruded PVC Pipes: What does it mean, and why is it important?



Your pipe and fitting compound formulation is at the heart of your operation and drives the success of the organisation and that of the piping system.

Chris Cheeseman, Technical Sales Manager at Akdeniz Chemson Additives Ltd. UK, will share his 30 years of PVC compound formulation experience, backed by his BSc (Hons) Chemistry & Polymer Science Technology degree.





Medium-Chain

Long-Chain







Presenter

SAPPMA Webinar IX

24 November 2021





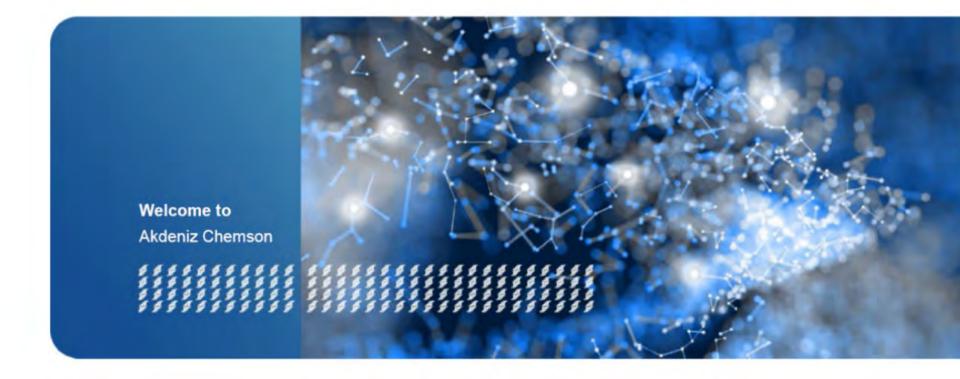
Chris Cheeseman

















1942

Our story began in 1942 Cookson plant in Sydney/Australia.

1986

German manufacturers Chemetall and the English Cookson Group merged. Chemson has born in Frankfurt, Germany. 2012-2013

Akdeniz Kimya joined Turkey's OYAK Group. One-year later, the Chemson Group became part of the OYAK Group as well.

1976

In 1976, Akdeniz Kimya was founded in İzmir, Turkey.

2000-2001

Chemetall moves the stabilizer business of its Brazilian subsidiary Chemetall to Brasil to the new company & in 2001 Chemson enters the Chinese market. 2020

Two strong brands merged into Akdeniz Chemson, and become the world market leader in PVC stabilizers.









Partnership with:









What is S PVC?



PVC is manufactured from two of the earths natural resources – Salt and Oil.

Salt provides the chlorine / Oil provides the ethylene

What is S PVC?



V.C.M is then mixed with water, peroxide catalyst and suspending agents



Depending on how long this is reacted a certain chain length/viscosity P.V.C (poly vinyl chloride) is produced.

S-PVC: Suspension Polymerisation

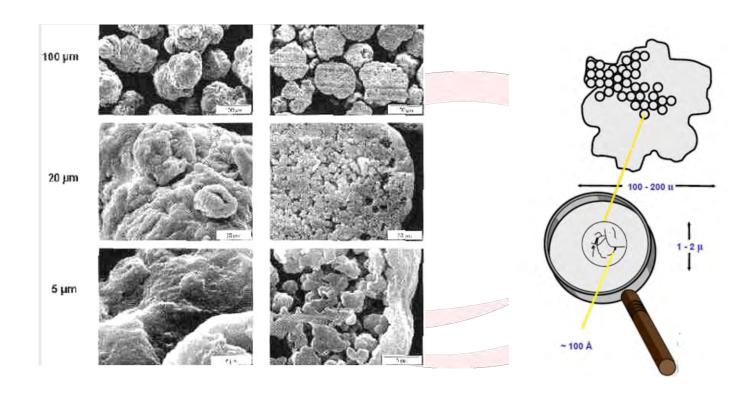


- > VCM (Vinyl Chloride Monomer) droplets are suspended in water in the presence of suspension agents.
- Heat and pressure is controlled to determine the chain length, and therefore the viscosity (K value)
- > In the presence of a catalyst, chains form within the droplets and remain in the lowest energy state: a ball known as a primary particle.
- > Primary particles agglomerate, and a skin is formed around these: These secondary particles are grains of resin



What does S PVC look like?







Why does PVC need stabiliser?



PVC is an unstable polymer (heat/UV/shear) and needs stabiliser to process it





Degradation of PVC

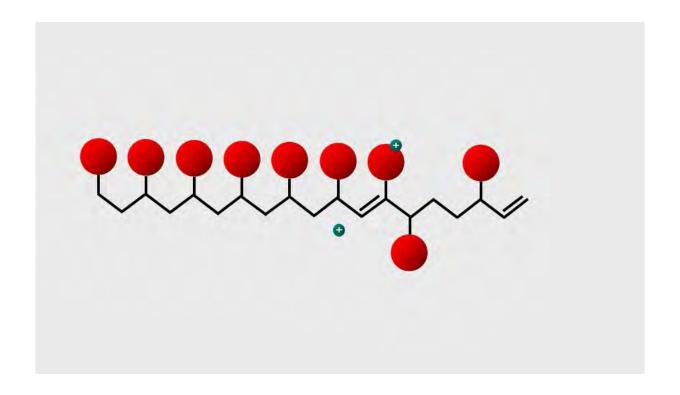






Degradation of PVC

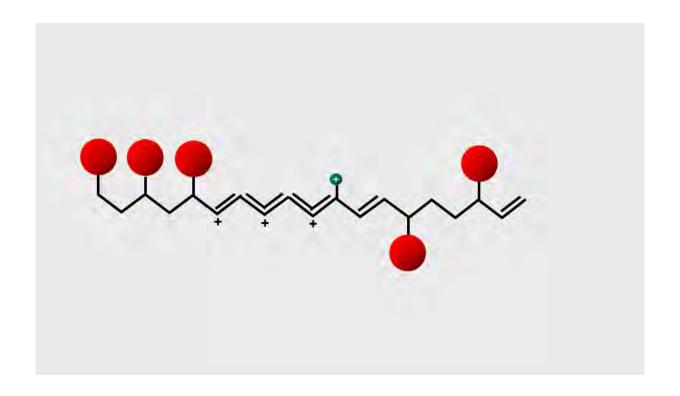






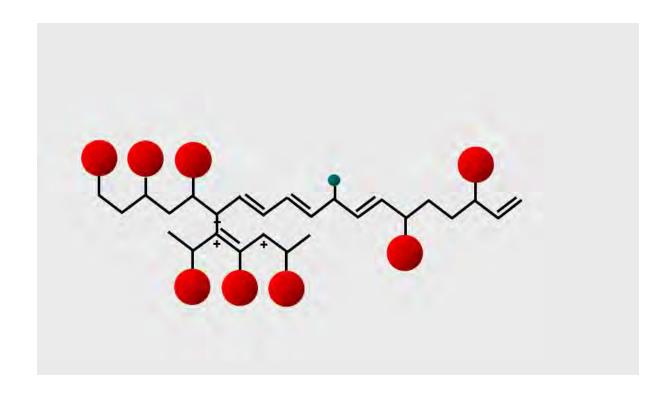
Degradation of PVC





Cross linking of PVC

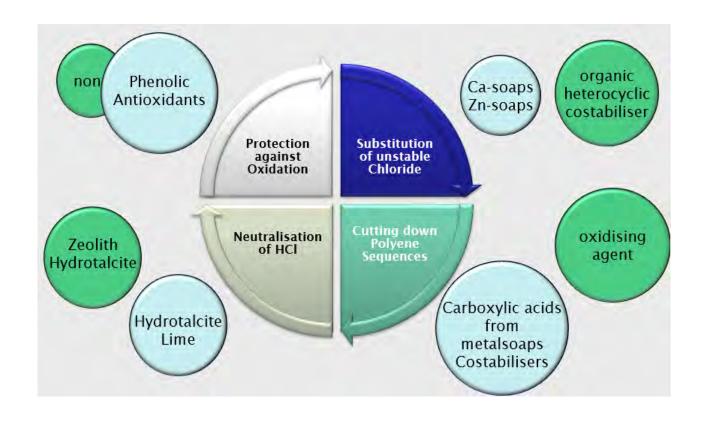






PVC Stabiliser Systems -Demands





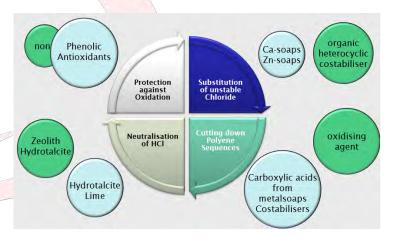


PVC stabiliser requirement



> Direct effect on PVC : enable processing

- substitution of labile Chlorine (Preventative)
- > neutralisation of Hydrochloric Acid (Suppressive)
- Reduction of degraded polymer chain :polyene sequences (Curative)
- prevention of (auto-)oxidation





PVC Stabiliser: composition



Ca/Zn Ca-organic

Substitution of unstable chloride

Zn soaps Org. heterocyclic co stabiliser

Reducing polyene sequences (double bonds)

Carboxylic acids from metal soaps oxidising agent

Co stabilisers: THEIC (Tris (2-hydroxyethyl) isocyanurate), Polyols, organo phosphites

Neutralising of HCI

Hydrotalcite, lime Zeolith, Hydrotalcite

Protection against oxidation

Phenolic antioxidants, HALS, UV stabiliser



Substitution of labile chlorine: ca/zn & ca- organic



- > Zn soaps substitute labile chlorine and improve the colour
- Due to the Lewis acid character heat stability is decreased
- Compensate this with synergistic complexing agents (co stabilisers)

$$Z_{n}(OOCR)CI + Ca(OOCR)_{2} \longrightarrow Z_{n}(OOCR)_{2} + Ca(OOCR)CI$$

Ca-organic uracil substitutes labile chlorine in a similar way, without a negative effect on heat stability

Reduction of polyene sequences: ca/zn



- > Polyene sequences are responsible for yellow discolouration
- > The greater the sequence the darker the colour
- > Metal carboxylates attach themselves to a double bond
- Initial colour and colour hold is improved



Acid Neutralisation



- > PVC starts to dehydrochlorinate above 70'C
- > HCI, if left unchecked, will become autocatalytic in degradation: use acid scavengers to react or absorb HCI
- > Mostly metal soap and mineral agents used in both systems
 - Calcium stearate
 - Hydrotalcite (Mg, Al hydroxycarbonate)
 - > Zeolite (Na-Al silicate)
 - > Brucite (magnesium hydroxide)
 - Chalk (calcium carbonate)
 - Lime (calcium hydroxide)



Prevention of (auto)-oxidation



- > Any polymer is subject to oxidation processes due to atmospheric oxygen. Increase in temperature increases the reaction.
- > Antioxidants are used in PVC to prevent autoxidation
 - Primary antioxidants are radicle scavengers, e.g phenols or amines
 - Secondary antioxidants remove organic hydroperoxides formed by primary antioxidants e.g phosphites
 - UV absorbers e.g benzophenones
 - Light stabilisers e.g HALS



PVC stabiliser one pack: process control



> immediate effect on the process

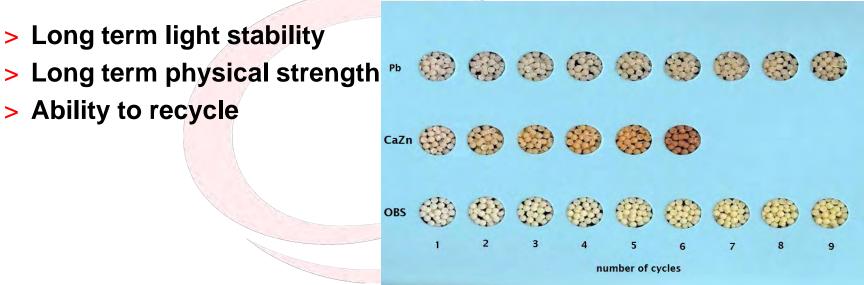
- point of gelation controlled by:
 - > Time, temperature and pressure
- > PVC melt viscosity
- Compatabilisation
- > Metal release effect



PVC Stabiliser : final product durable



- > Stabilisers also have a part to play after the extrusion process
- > Long term light stability
- Ability to recycle





PVC Stabiliser one pack: Pipe requirements Akdeniz Chemson



> Pressure pipe: focus on static thermo-stability

- Long residence time of material in the die head and down stream
- Thick walled pipes cool slowly and have a relatively smaller inner surface area.
- Less external lubrication required due to lower back pressure and higher demand on gelation-critical to withstand high pressure.



Ca-organic pipe 1200 x 23.6mm



PVC Stabiliser one pack: Pipe requirements Akdeniz Chemson



- > Sewer & waste water pipes: focus more on dynamic stability
 - Lower gap width of nozzle leads to higher back pressure
 - High output and faster screw rotation leads to more friction
 - Higher filler levels leads to higher stiffness and viscosity
 - Need for high external lubrication

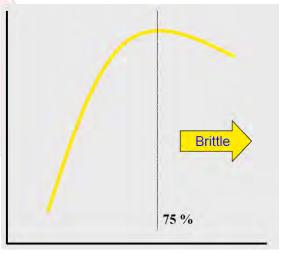




Lubricants: important process control

- > Lubricants help to create a homogenous melt
 - > Poor homogeneity undispersed particles/ agglomerates > mechanical properties
- > Lubricants help achieve the correct level of gelation
 - > 75% gelation is optimum
 - > below this : poor physical performance
 - > Above this: reduction of physical performance
 - Increase dehydrochlorination > colour

Mechanical properties



Gelation

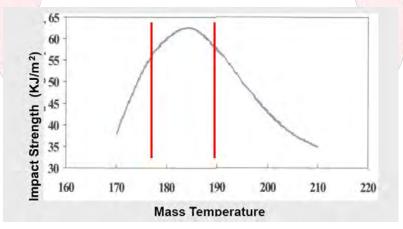


Lubricants important process control



Over processing, not just a PVC issue:

- Impact modifier added to PVC to help overcome mechanical issues also has a processing window
- > CPE (chlorinated polyethylene) shown here has a narrow processing window. Excessive temperature leads to increase crystallinity
- Crystallinity can develop over time as the pipe cools and impact strength, whilst initially was good, can deteriorate.





Effect of lubricants on PVC

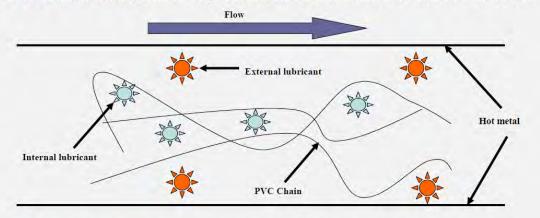


- > Polar lubricants are compatible with PVC= Internal lubricants
- > None polar lubricants incompatible with PVC =External lubricants

Lubricants: important process control



Internal lubricants are required to increase chain mobility and reduce shear in the PVC matrix during processing. These products need to be compatible with PVC.



External lubricants are required to prevent the chains sticking to hot metal surfaces during processing. These products need to be in-compatible with PVC.



Lubricants: important process control



Fischer Tropsch paraffin wax:

- > Most effective external lubricant
- > Positive influence on surface gloss
- > Delays gelation and decreases motor load

>Polyethylene Wax:

- > Effective especially in the tool
- > Decreases back pressure
- > Good metal release



Lubricants: important process control



> Fatty Ester waxes:

- Decrease melt viscosity- especially for injection moulding and corrugated pipes
- > Decrese melt pressure, with no negative influence on gelation

Oxidised Polyethylene waxes:

- Very effective booster of gelation
- > High own viscosity
- > Negative influence on surface gloss



Rheology: processing of PVC



In the extruder, the PVC dry-blend is subject to heat from the barrels and shear from the screws. This causes the powder to melt (gel). Where on the barrel this occurs is controlled by the lubrication of the stabiliser one-pack. When the PVC reaches the adapter it should be a fully gelled homogeneous melt (180-190 degC).

Plastification

Plastification

Feed

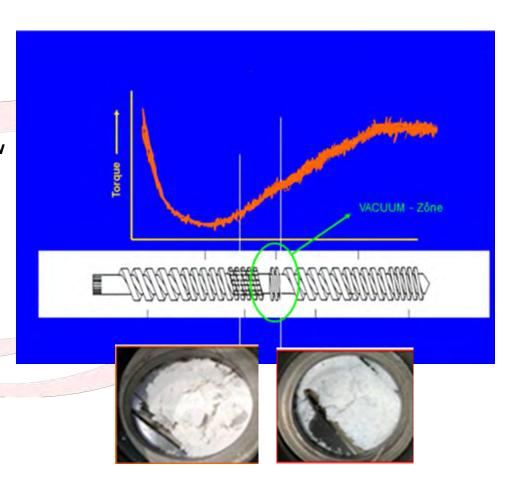
Plastification



Rheology: slow gelation issues



- > No de-venting of moisture or volatiles
- > Risk of powder blocking vacuum
- > Poor mechanical properties
- Usually low torque
- Usually low melt temperature
- > High die pressure: increased back flow
- Dimensional issues
- > Lower output
- Risk of burning





Rheology: Over gelation



Poor de-venting (trapped moisture and volatiles)

Over gelation, poor physical performance

Usually high torque

Usually high melt temperature

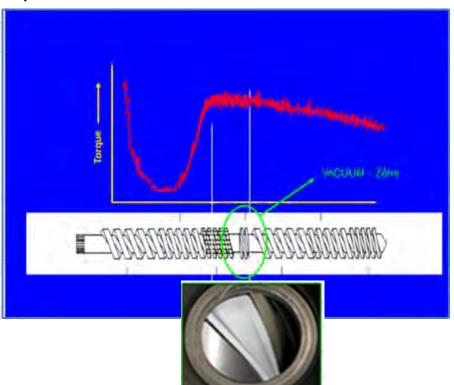
Dimensional issues

Wavy inner surface

Possible burning

Discolouration

Risk of Plate out

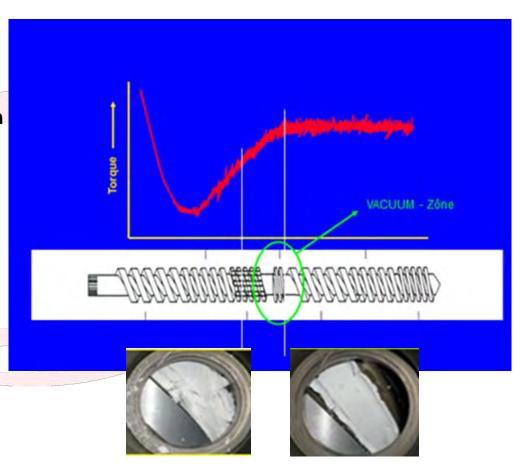




Rheology: ideal gelation



- Material has started to fuse at the vent
- > Little risk of blocking the vacuum
- Volatiles and moisture can be withdrawn
- Processing is under control





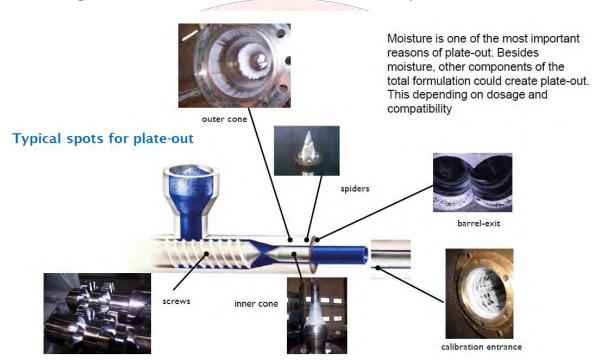
Moisture issues



Moisture is always present in dry blend

Good aspiration is required in the mixing plant

Poor de-venting: moisture still in the melt can lead to plate-out





Moisture issues





Rheological issues



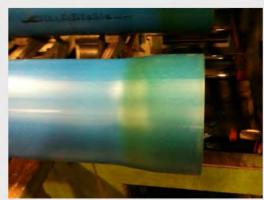


Die sticking



Static and dynamic stability issues





Insufficient static stability More effective primary stabiliser



Burning due to sticking to the screw Different lubrication system



Insufficient dynamic stabiliser More effective primary stabiliser And lubricant system

Insufficient static- dynamic stabiliser



Colour stability



Critical for thick walled applications
And the use of different extruder types (friction)
Increase primary stabiliser and co stabiliser



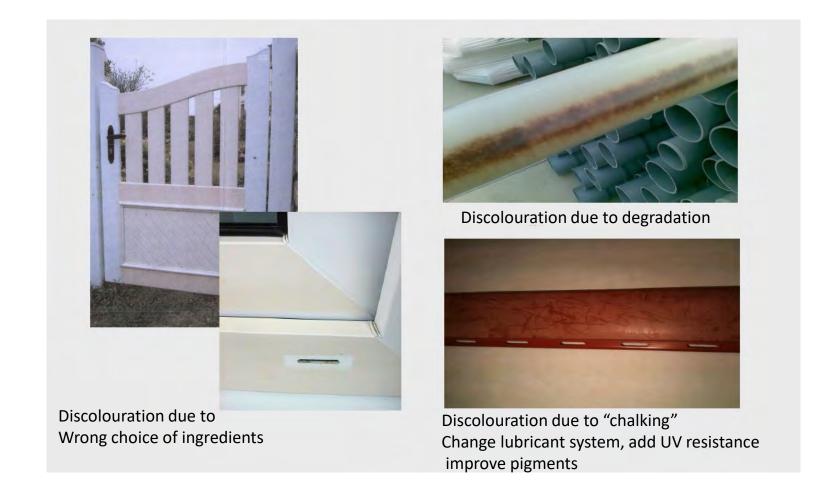
300mm rod





Light stability





Summary



- PVC's dipolar nature gives it the ability to be combined with a wide range of ingredients to alter the end application from flexible film to rigid pipe
- Achieving the correct level of gelation is critical to PVC performance
- > Stabiliser one packs allow processors to achieve this
- Correct balance of ingredients can help open up a broader processing window, even on challenging products



Akdeniz Chemson







Questions and Answers









Chris Cheeseman

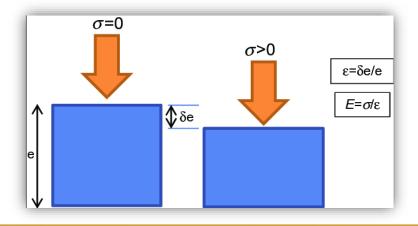






Remember it all needs to add up

The product is the sum of all its components



Implementations of Two-level Logic Sum-of-products - AND gates to form product terms (minterms) - OR gate to form sum · Product-of-sums - OR gates to form sum terms (maxterms) - AND gates to form product

Your Strength is a function of your Stress and Strain

Allow us to look into your Stresses and Strains



Synergies come from joining strengths we often do not think of















Questions and Answers







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