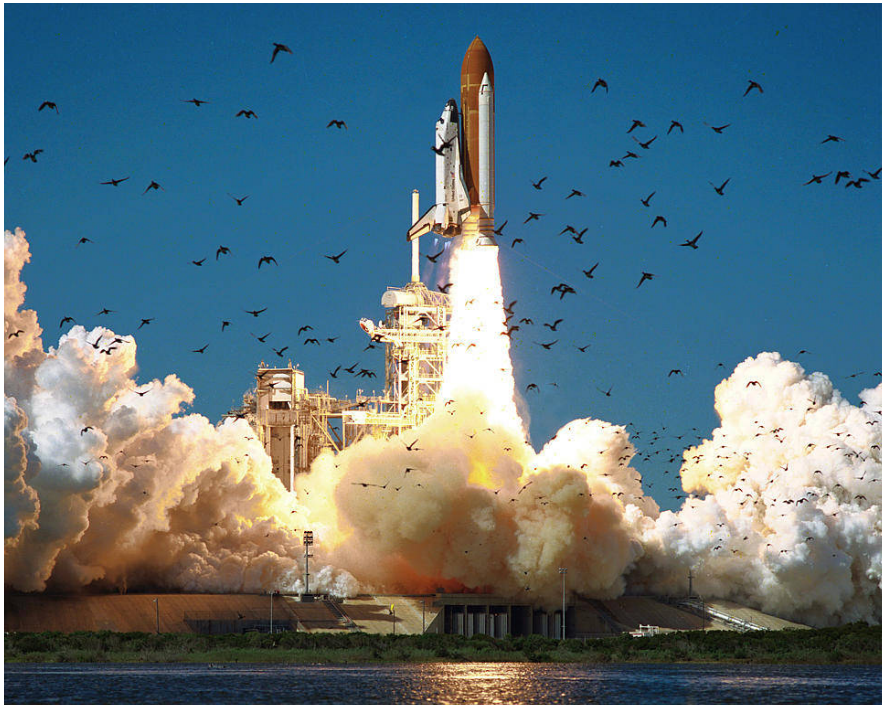
RUBBER IN SPACE

Yes, it is rocket science……



Bryan Willoughby, Independent Consultant

STRUCTURE OF THE TALK

- Start with the Conclusions
- Then some scary chemistry (sorry)
- Finally answer the question
  “did the race to the moon give
  us non-stick frying pans?”

KNOW YOUR MATERIALS

Challenger – Jan 28th 1986

“For a successful technology, reality must take precedence over public relations, for nature cannot be fooled”

Richard Feynman

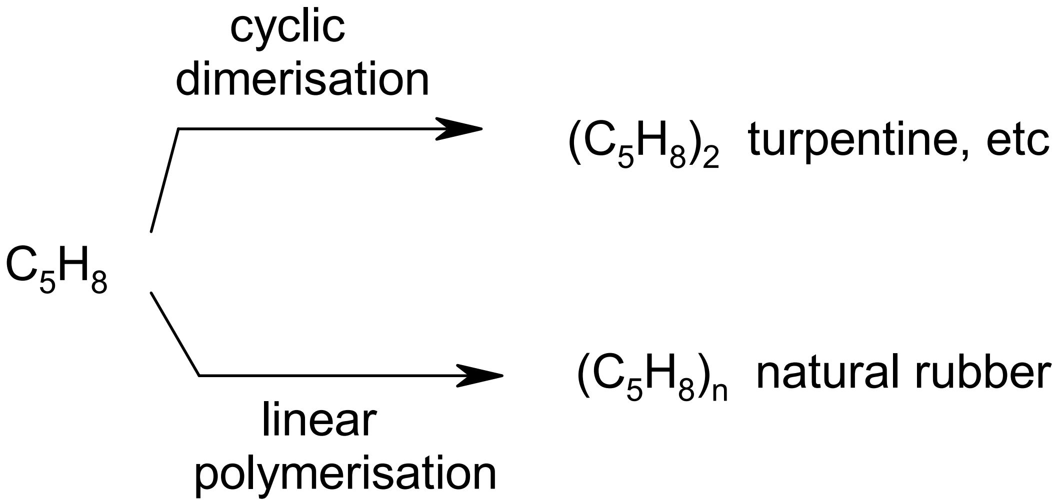
NATURE HAS ITS WAYS…..

Plants produce isoprene
$CH_2{=}C(CH_3){-}CH{=}CH_2$
…….at some cost in energy.

Not clear why – but it is possible they do it to combat heat stress and to protect themselves from reactive oxidising species.

Isoprene is very easily oxidised

ISOPRENE IS QUITE REACTIVE



C_5H_8

cyclic dimerisation

$(C_5H_8)_2$ turpentine, etc

linear polymerisation

$(C_5H_8)_n$ natural rubber

- **Products are also oxidisable**
- **Turpentine used to accelerate oxidation in drying oils**
- **Oxidation of natural rubber exploited in vulcanisation**

WITHOUT VULCANISATION, RUBBER IS CREEPY AND TACKY

Unvulcanised rubbers make good contact adhesives

- – but not much else

Vulcanisation by oxidation can be achieved with sulphur or peroxides

– e.g. simplistically

$$\text{Rubber-H} + S_x + \text{H-Rubber} \longrightarrow \text{Rubber-}S_y\text{-Rubber} + H_2S$$

$$\text{Rubber-H} + [O] + \text{H-Rubber} \longrightarrow \text{Rubber-Rubber} + H_2O$$

VULCANISATION OF NR

- 1839 – Charles Goodyear discovered vulcanisation with sulphur
  - 8 phr sulphur in NR – ca 6hr at 140°C

- Metal oxide (ZnO) activation
  - 5 phr ZnO/8 phr S – ca 5hr at 140°C

- 1906/7 – first organic accelerators (aniline, thiocarbanilide)
  - 2 phr aniline/5 phr ZnO/6 phr S – ca. 3 hr @ 140°C

- 1919 – thiuram accelerators

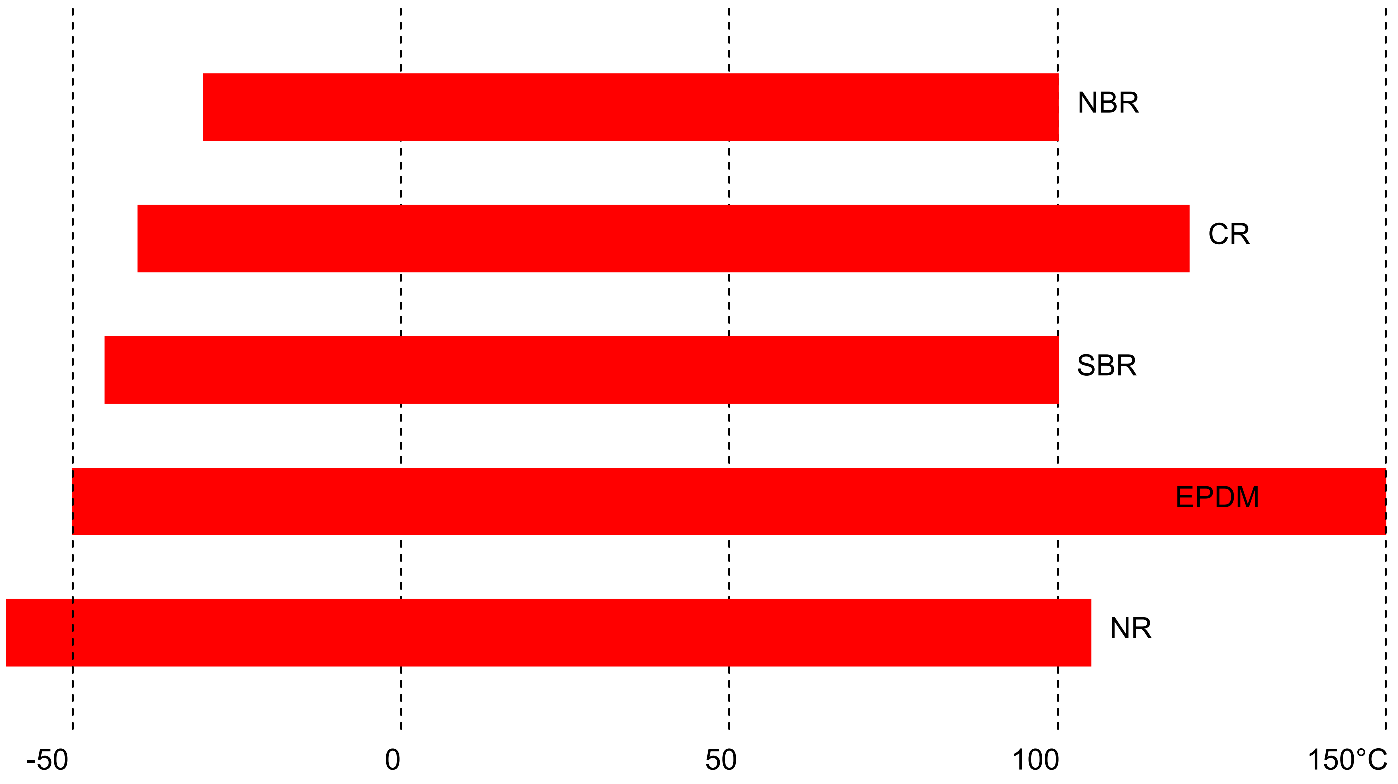
- 1925 – thiazole accelerators & start of mass production of tyres
  - now 30 minutes or less @ 140°C

- 1937 – delayed action (sulphenamide) accelerators

EARLY SYNTHETICS – VULCANISED BY OXIDATION (SULPHUR OR PEROXIDE)

- **1911 – Methyl rubber (polydimethylbutadiene) at Bayer & Co in Germany**
- **1926 – Butadiene rubber at I.G. Farbenindustrie.**
- **1927 – Polysulphide rubber (by Joseph Patrick trying to make antifreeze!)**
- **1927 – Emulsion polymerisation of butadiene/start of work on copolymers**
- **1932 – Chloroprene rubber production started at Du Pont**
- **1934 – Nitrile rubber production started at I.G. Farbenindustrie**
- **1937 – SBR production started in Germany (1942 in the US)**
- **1942 – Butyl rubber production at Standard Oil (NJ)**
- **1952 – Ziegler catalysis and beginnings of stereo rubbers (EPDM, etc)**

OXIDISATION USUALLY LIMITS UPPER SERVICE TEMPS



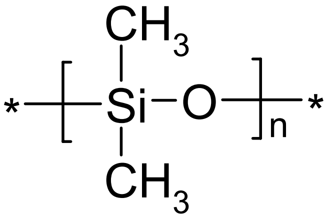
ROCKETS BRING THEIR OWN OXIDISERS – e.g. LIQUID TYPES

- **LOX – Liquid oxygen**
- **NTO – Nitrogen tetroxide, N_2O_4**
- **Nitric acid – HNO_3**
- **IRFNA – Inhibited red fuming nitric acid (14% N_2O_4 in HNO_3)**

How many oxidisable rubbers will stand up to these?

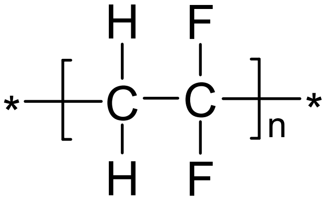
REDUCE AVAILABILITY OF OXIDISABLE HYDROGEN

For better resistance to oxidation



$*-[Si(CH_3)_2-O]_n-*$

Silicone - low abstractability of 1^{ry} H



$*-[CH_2-CF_2]_n-*$

VDF co-polymers -abstractability of H limited by nearby fluorines

or remove H completely……

SILICONES AND FLUOROELASTOMERS

- 1944 – Commercial production of silicones (General Electric)
- 1953 – Fluorosilicone from Dow Corning - Silastic LS (LS = “low swell”)
- 1955 – VDF/CTFE copolymers from M W Kellogg & 3M (Kel-F)
- 1957 – VDF/HFP copolymers from Du Pont (Viton A).
- 1958 – VDF/HFP copolymers from 3M (Fluorel)
- 1960 – VDF/HFP/TFE terpolymers from Du Pont (Viton B, F, etc.)
- 1975 – TFE/C_3H_6 copolymers from Asahi Glass
- 1975 – VDF/PFMVE/TFE terpolymers from Du Pont (Viton GLT)
- 1975 – TFE/PFMVE copolymers from Du Pont (Kalrez)

VDF = vinylidene fluoride, CTFE = chlorotrifluoroethylene, HFP= hexafluoropropylene, TFE = tetrafluoroethylene, PFMVE = perfluoromethylvinyl ether)

LIQUID FUELS FOR ROCKETS

- **LH2 – Liquid hydrogen**
- **RP-1 – Refined kerosene**
- **Hydrazine – H_2NNH_2**
- **MMH – Monomethylhydrazine, $HMeNNH_2$**
- **UDMH – Unsymmetrical dimethylhydrazine, Me_2NNH_2**
- **50:50 Hydrazine:UDMH (Aerozine 50)**

Organic bases attack rubbers containing S−S, Si−O, and VDF copolymers

SILICONES AND FLUOROELASTOMERS

Silicone MQ, PMQ, VMQ
Poor fuel resistance, but wide operating temp range, good resilience & dielectric strength
– used in aerospace wiring

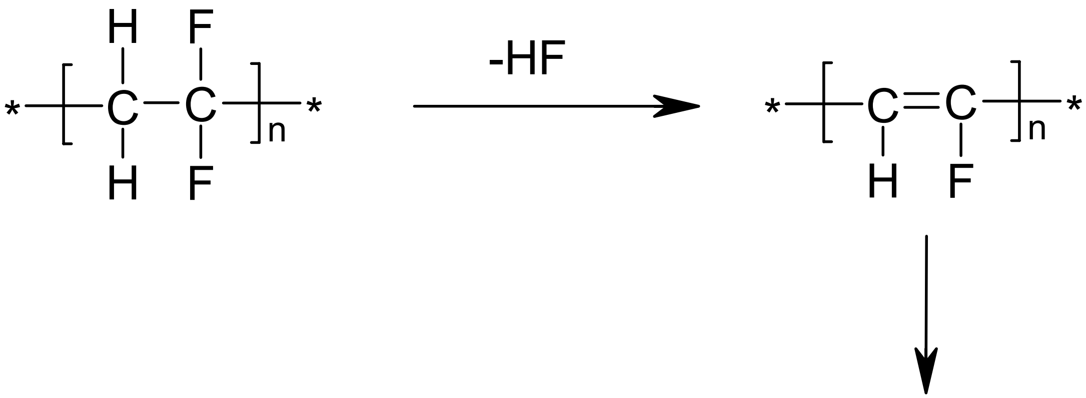
Fluorosilicone FMQ, FVMQ
As silicone, but with 36.5% F for better (jet) fuel resistance – used in aerospace hoses & seals

VDF polymers FKM, FPM, CFM
More F than fluorosilicone (>65%) for better resistance to various fluids
– used in aerospace hoses and seals – seals well against hard vacuum

TFE/C_3H_6 polymers TFP, FEPM
54% F – better resistance to organic bases than FKM

Perfluoroelastomer FFKM (e.g. Kalrez)
V. Expensive – Performance to >300°C, withstands hydrazines & oxidisers

EXPLOIT THERMAL BREAKDOWN TO VULCANISE VDF COPOLYMERS



Cure with diamine or bisphenol

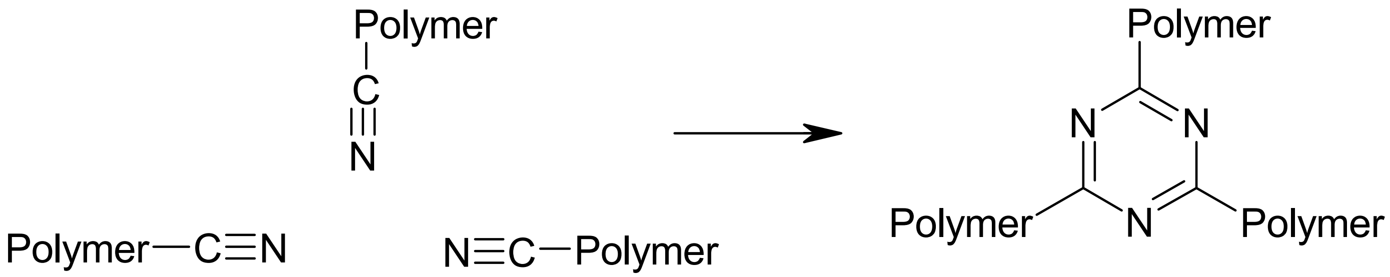
Service to >200°C, but still not fully resistant to N_2O_4

Also attacked by organic bases

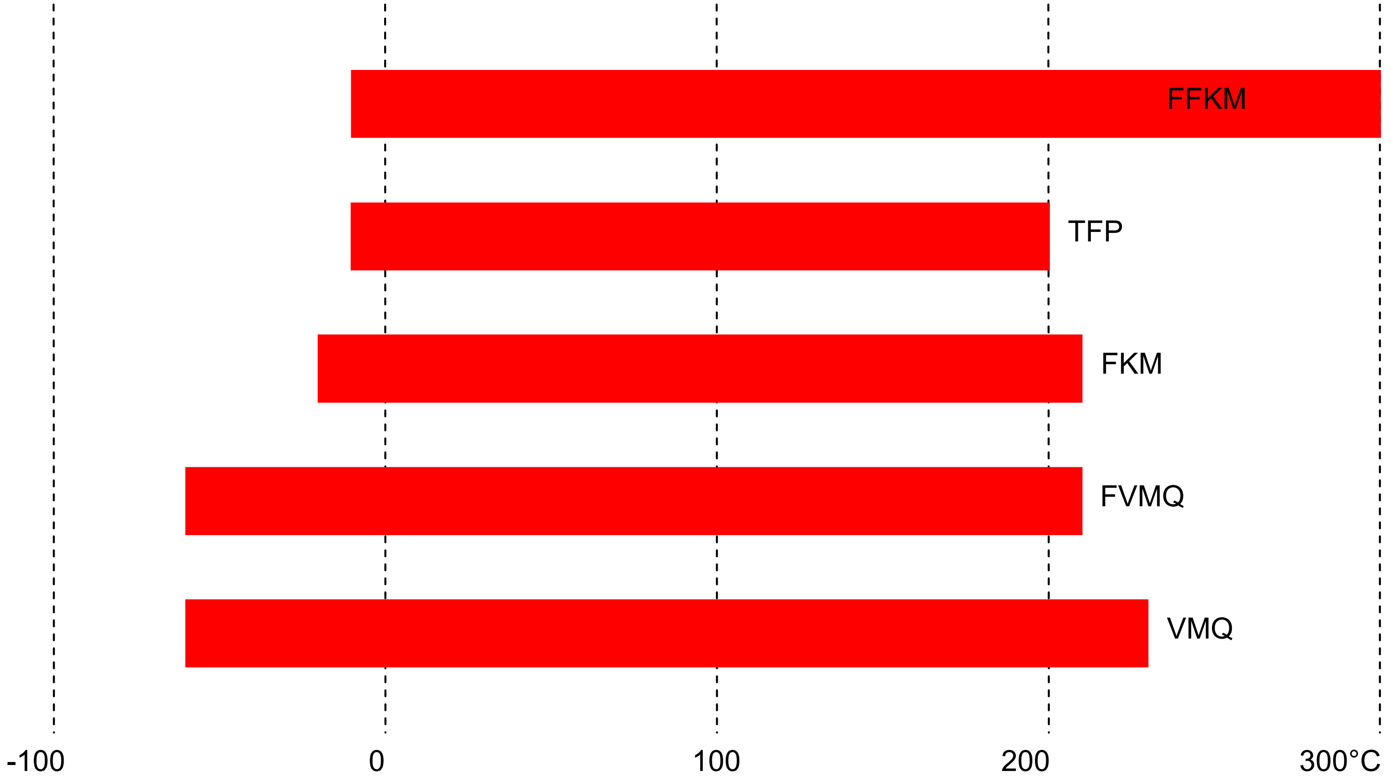
Fluorocarbon chain stiffer than hydrocarbon – low temp performance suffers

NEED THIRD MONOMER FOR FFKM TO EFFECT CURE (PROPRIETARY SYSTEMS)

- Various systems
- Best high temp performance with nitrile → triazine cure (organotin catalyst)
- Use third monomer such as $CF_2{=}CFO(CF_2)_4CN$



TYPICAL SERVICE TEMP RANGE SILICONES & FLUORELASTOMERS



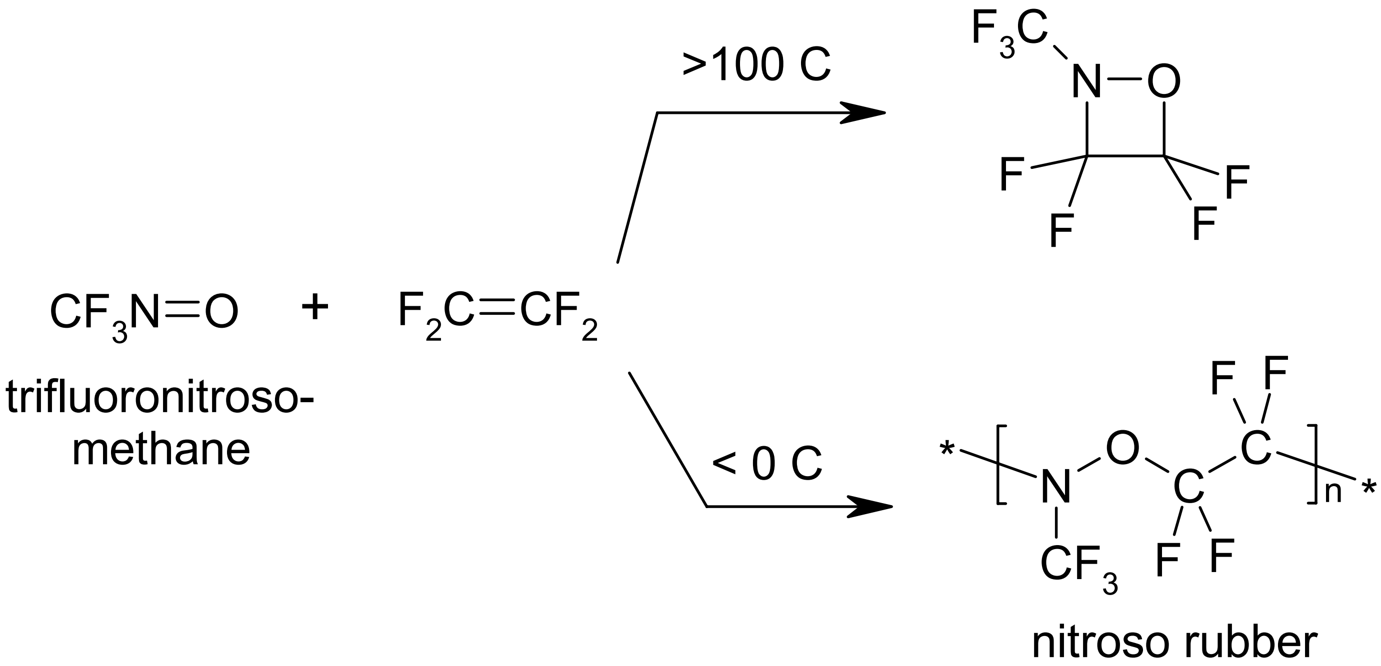
KNOW YOUR MATERIALS

Challenger – v cold that day.

Failure of a joint seal (incorporating FKM O-ring) on solid rocket booster directed flame to LH2 tank

Remedy – redesign the whole seal for less movement and incorporate back-up O-ring

NITROSO RUBBER – CAMBRIDGE 1955 (BARR & HASZELDINE)



TRIFLUORONITROSOMETHANE

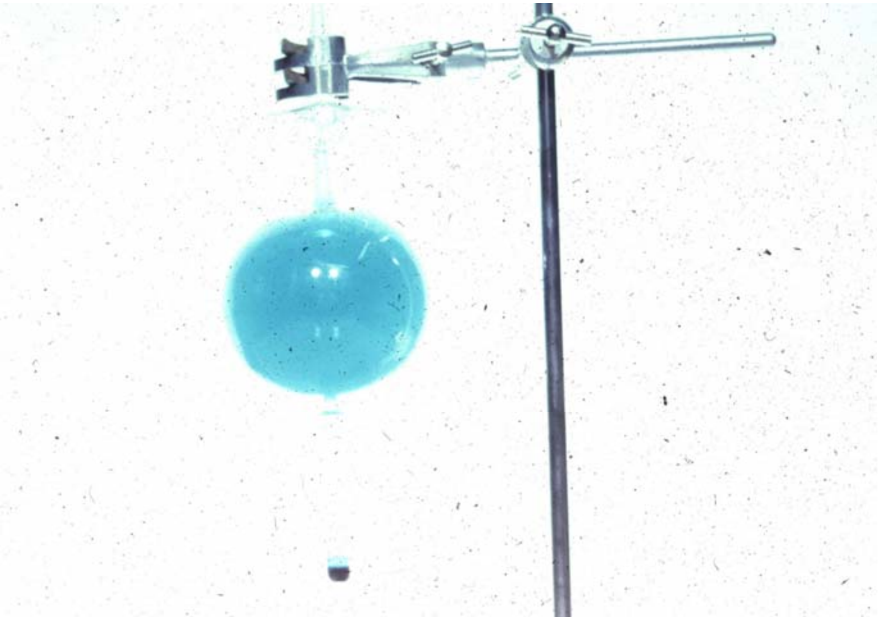
CF_3−N=O

Bp -85°C

Blue gas at RT

C_2F_4

Bp - 76°C



……. handling these will be interesting!

THIRD MONOMER FOR CURABLE NITROSO RUBBER – UK (UMIST) ROUTE

$CF_3N{=}O$ + $CF_2{=}CF_2$ + $CF_2{=}CFC({=}O)F$

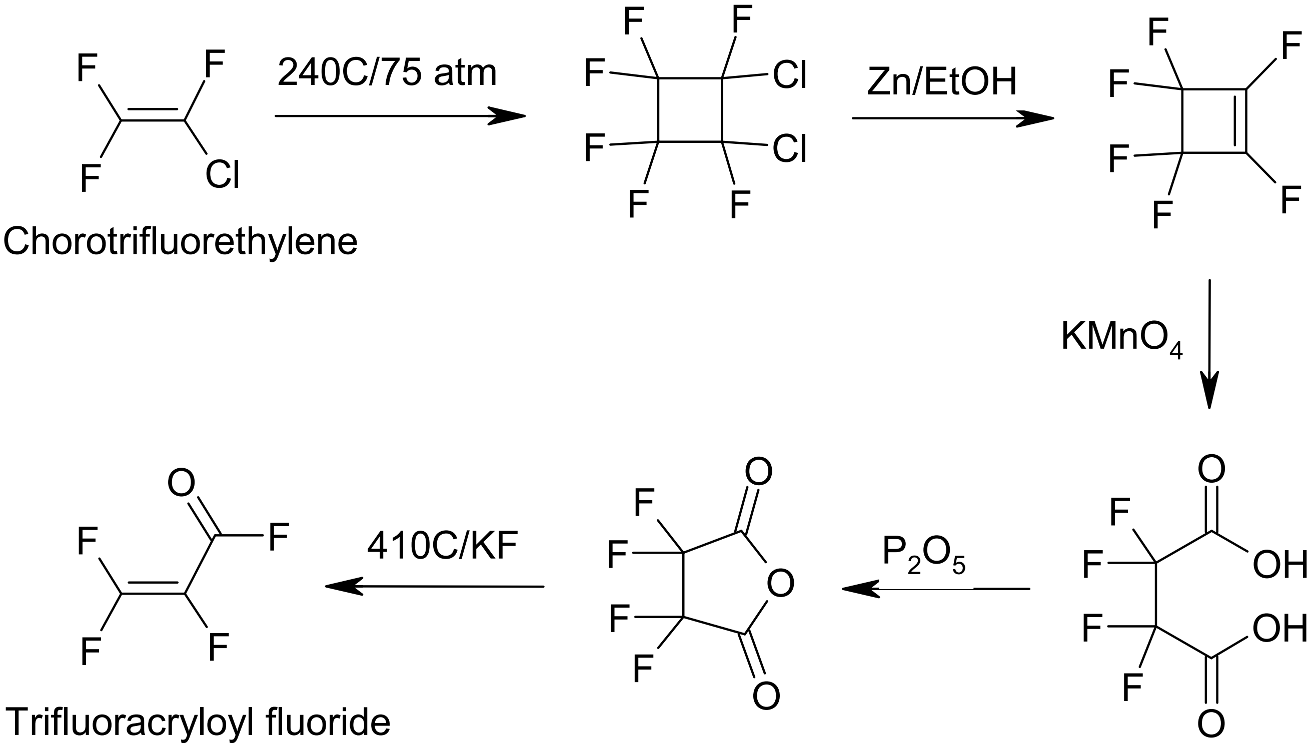
Bulk polym. at 0°C

Fractionate polymer with CF_2ClCF_2Cl & acetone

$H_2N(CH_2)_6NH_2$ at RT

Crosslinked rubber, T_g -52°C

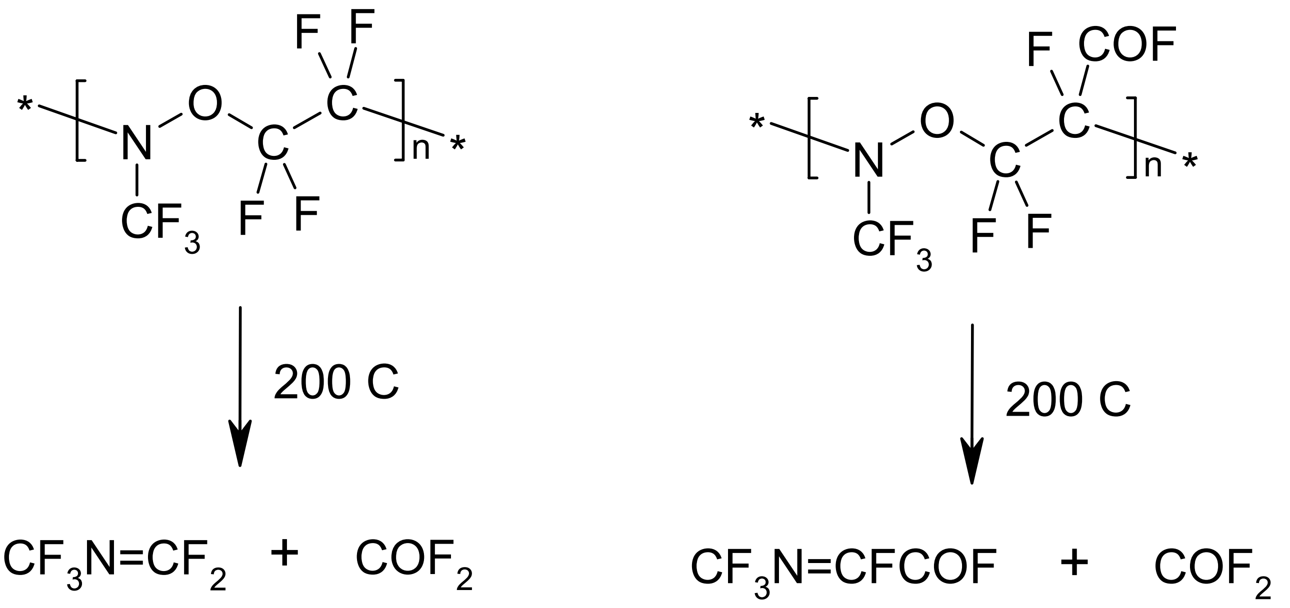
FIRST CATCH YOUR MONOMER



Chorotrifluorethylene

Trifluoracryloyl fluoride

HAVING GOT YOUR POLYMER – DEGRADE IT

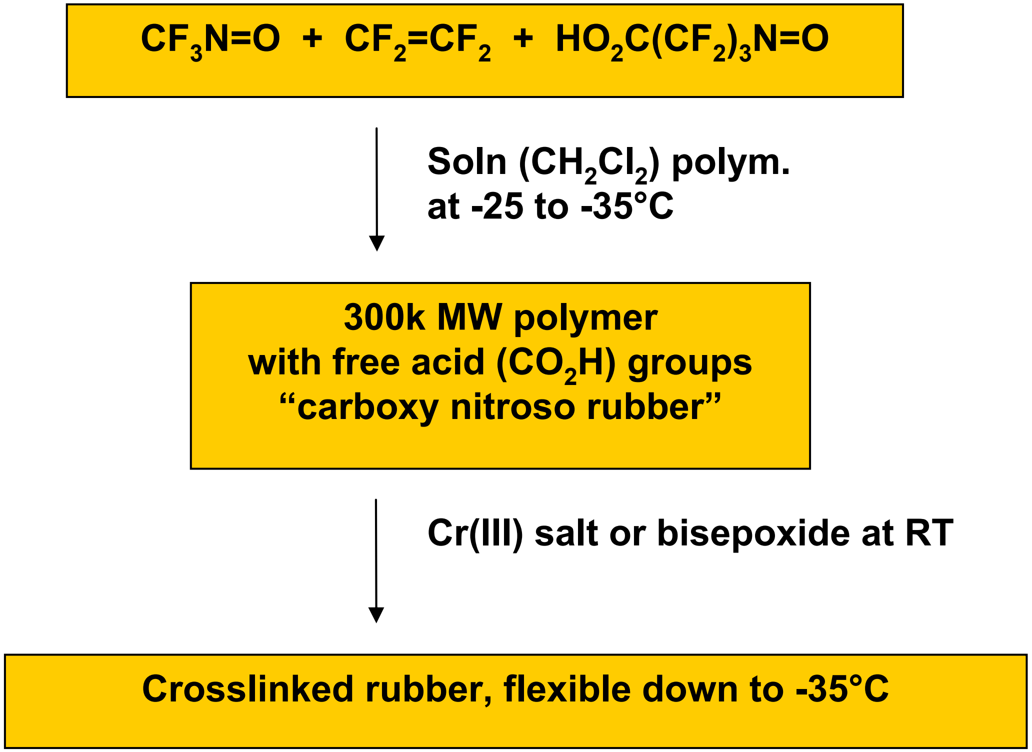


$CF_3N{=}CF_2$ + COF_2

$CF_3N{=}CFCOF$ + COF_2

Nobody told me why……..

THIRD MONOMER FOR CURABLE NITROSO RUBBER – USA (THIOKOL) ROUTE



$CF_3N{=}O$ + $CF_2{=}CF_2$ + $HO_2C(CF_2)_3N{=}O$

Soln (CH_2Cl_2) polym.
at -25 to -35°C

300k MW polymer
with free acid (CO_2H) groups
"carboxy nitroso rubber"

Cr(III) salt or bisepoxide at RT

Crosslinked rubber, flexible down to -35°C

KNOW YOUR MATERIALS – APOLLO 1

- 27th January 1967, a fire in the command module generated such intense heat that it took 6 minutes for technicians to open the hatch. The crew inside were killed
- Apollo command module has a pure oxygen atmosphere
- Enquiry was shocked by the combustability of various rubbers & plastics present
- Asked for a rubber which wouldn't burn in pure oxygen

CARBOXY NITROSO RUBBER PUT A FOOTPRINT ON THE MOON

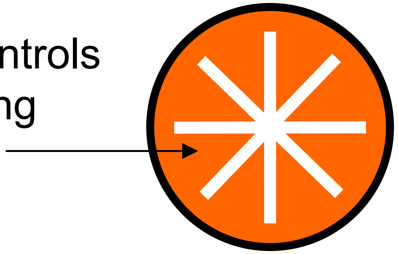
- Cure CNR with Cr trifluoracetate or dicyclopentadiene diepoxide
- Physical properties between FKM and FMQ
- Exceptional resistance to IHRFNA & N_2O_4
- CNR is non-combustible in pure oxygen
- Gives off its own fire extinguisher on heating
- Used in space suits on Apollo missions
  - Coatings on fabrics
  - Soles of boots

MOST RUBBERS GIVE OFF A FUEL ON HEATING

- Polysulphide especially good at this
- Gives off cyclic ethers/disulphides
- Liquid polysulphides cure by oxidation
- Use polysulphide as fuel, and curative as oxidant for a solid rocket propellant
- Ammonium perchlorate + liquid polysulphide gives a castable rubber for a solid rocket motor
- Motor based on Thiokol LP-2 used in the US Sergeant (surface-to-surface) missile

SOLID ROCKET MOTOR

- FUEL AND OXIDISER MIXED TOGETHER



Solid propellent usually cast in star shape – geometry controls rate of burning

Outer (metal) casing has insulating rubber layer (usually EPDM).

Between this and the propellant is a liner (e.g. based on binder) to minimise risk of adhesive failure.

The one you can't switch off….

POLYURETHANES BURN WELL ALSO

- For added impulse just use PU as a binder
- Polaris A1 uses Al powder as fuel and ammonium perchlorate as oxidiser
- Create slurry in (liquid) PU, cast in place and allow to cure

FOR MORE IMPULSE USE POLYDIENE-PU AS BINDER

$$HO{-}(CH_2{-}CH{=}CH{-}CH_2)_n{-}OH$$

- Hydroxyl-terminated polybutadiene
- Available as Polybd® R45 HTLO from Sartomer
- Liquid polymer (2800 MW), 8000 mPa.s viscosity
- Low viscosity allows for high solids loading
- Functionality ca. 2.5, cure with a diisocyanate
- Well characterised system in sold propellants

OTHER SOLID PROPELLANT BINDERS

Acid (CO_2H) functional binders cure with epoxies and avoid toxicity of NCO

CTPB	Carboxyl-terminated polybutadiene
CTBN	Carboxyl-terminated polybutadiene-acrylonitrile
PBAA	Prepolymer of butadiene-acrylic acid
PBAN	Prepolymer of butadiene-acrylic acid-acrylonitrile

SPACE SHUTTLE

- Solid booster rocket Al/Ammonium perchlorate + PBAN
- Stage 1, LH2/LOX
- Orbital manoeuvring system – MMH/NTO
- Reaction control system MMH/NTO

OUTCOMES FROM PUTTING A MAN ON THE MOON….

- Environmental awareness
- "Zero error engineering"
  – e.g. reliable cars

PTFE was discovered in 1938

It was subsequently developed for the Manhattan Project – not Apollo