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# SUBSTITUTION EFFORTS IN CNES

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CNES

ESA REACH WORKSHOP

19 JUNE 2024

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# CNES ACTIONS TO HANDLE REACH REGULATION AT MATERIALS AND PROCESSES LEVEL

## Risks anticipation and management

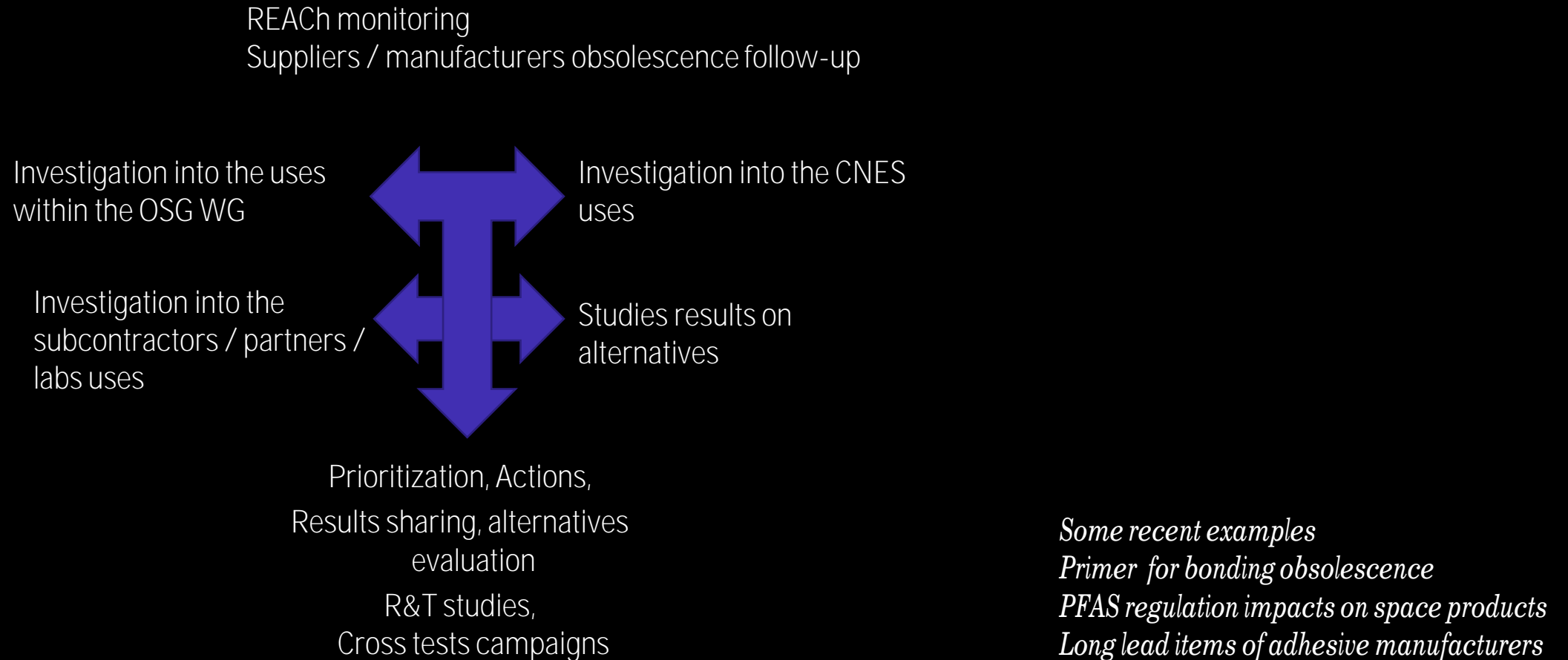
- Materials and processes risks monitoring and identifying
  - MATREX (Internal CNES materials database)
- Support of CNES projects and users with a dedicated person
- R&T activities and new materials / technologies development
- Validation of new materials, processes and manufacturing technologies

## Communication / training

- Internal materials users: building of an internal network
- Projects partners: SME, scientific labs
- Information sharing / regulation follow-up
  - Participation to MPTB: industrials, agencies network
  - Participation to technical working groups relative to materials and processes: Obsolescence splinter group, Lead Task Force, restriction task force

# CNES ACTIONS TO HANDLE REACH REGULATION AT MATERIALS AND PROCESSES LEVEL

Obsolescence splinter group: Communication network with European agencies and industrials



# CNES ACTIONS TO HANDLE REACH REGULATION AT MATERIALS AND PROCESSES LEVEL

CNES internal training on REACH regulation and requirements for projects and partners

## Explaining REACH status for substances

- Annex XIV substance for CNES use, no authorisation = no use  
Recommendation, requirement to substitute



- Candidate list, SVHC,  
Use allowed without REACH restrictions (pay attention to worker protection, QSE policy) but with regulatory declaration requirements and follow-up of substance status
- Substance impacted with restrictions (Annex XVII)  
No restriction if not concerned with cases described in Annex XVII.

## Explain article 33 requirements and risks

- Tips to handle article 33,  
Support for project as early as possible  
Still some challenges: re-delivery, out of Europe manufacturer, article definition



# CNES ACTIONS TO HANDLE REACH REGULATION AT MATERIALS AND PROCESSES LEVEL

## *Space impacted substances*

### Annexe XIV

- 46 space materials impacted/ 114 space materials to be impacted soon
- Short term: wider technical domain since metallic salts included (lead, nickel....) from surface treatment to electronics and paints.
- Early activities lead from 2013 with CNES R&T program and ESA activities: for surface treatment, alternatives identification, assessment, requirements revision and validation tests adaptation (humidity vs salt spray test)

Important impact managed by space industrials:

- ✓ Product validation and process verification with one or more suppliers
- ✓ re-validation of related processes: coatings, adhesive bonding

# CNES SUBSTITUTIONS ACTIVITIES

CNES R&T activities: support of French industrials

- Replacement of REACH impacted resins by 3D PLUS

- R&T “Fatigue modelling of lead-free solder joints”

- Elemca
- Goal : acceleration model for lead-free board level assemblies
- Content : Fatigue lifetime tests, failure mechanism characterization, finite element analysis
- Progress : ongoing thermal cycling test and finite element analysis

- Evaluation of EPIG Finish for PCB

- ADS
- Status : R&T closed in March 2024
- Evaluation according to ECSS-Q-ST-70-60C and ECSS-Q-ST-70-61C of a new surface finish for PCB lead free compatible and without Ni
- Compliant results but limited availability of the EPIG finish for the moment



# CNES SUBSTITUTIONS ACTIVITIES

CNES R&T activities: support of French industrials

*Evolutions of concern regarding the domains impacted  
Initially surface treatments, paints (aqueous), propellants  
Growing impact in electronics*

## - Low loss PCB

- TAS
- Status : tests vehicles manufacturing on going
- Evaluation according to ECSS-Q-ST-70-60C of new high speed dielectric materials and 4 surface finish lead free compatible and without Ni

CNES participation (advisory board) to European Project - Horizon Europe « LEad-free Transition for The EuRoPean Space Sector » = LETTERSS

- Scalian, REACHLAW, Airbus, TAS-FR, TAS-ES, TESAT, SODERN, ALTER, HTV, TU Darmstadt, IRT Saint Exupéry
- Goal : reliable lead-free processes for space electronic assemblies, acceleration model for board level assemblies, use of COTS in space electronic assemblies, study of tin whisker growth mechanism
- Content : soldering process optimization, verification of assemblies, fatigue lifetime tests, failure mechanism characterization, whisker growth characterization
- Progress : state of the art, selection of test conditions

# CNES SUBSTITUTIONS ACTIVITIES

On a practical level, CNES has also labs and integration activities on Toulouse site.

Identification of CMR products and replacing actions

- Follow-up of CNES labs:
  - Security visit by Health, Security and Environment section: products survey and substitution actions
- Procedure for introducing new products on site (dedicated CNES procedure) includes analyses of REACh Annex 14 and 17, safe use in conformity with SDS
- Dedicated studies

- ▶ ECSS-Q-ST-70-05C : Solvents and reference standards with reduced environmental impact

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Martin Loesch (intern), Sabine Dagrás – ADS Toulouse



## MOTIVATION

organic solvents (alcohols, ketones, hydrocarbons...) widely used for different applications:  
degreasing, cleaning, analysis (molecular contamination monitoring)

Major drawbacks: emission of VOCs and potential CMR (Carcinogenic, Mutagenic, Reprotoxic) substances



Example: ECSS-Q-ST-70-05C Detection of organic contamination of surfaces by infrared spectroscopy (FTIR) protocols with **2 CMR substances**:



bis (2-ethylhexyl) phthalate\* as reference standard  
CMR cat. R1B - REACH non compliant (annex XIV)

➔ for calibration in order to quantify the surface molecular contamination levels

Chloroform as solvent of contaminants  
CMR cat. 2 - REACH restrictions (annex XVII)

Indirect method – wiping process

*“Cleaning can be performed by Soxhlet extraction or immersion in chloroform.”*

Calibration

*“For the preparation of the stock solution, chloroform of spectroscopic grade, having a non-volatile residue (NVR) < 5 µg/g, is used.”*

Cleaning of witness plates

*“Clean the witness plate with a tissue and chloroform.”*

Contact test

*“Clean the aluminum plates with the syringe containing chloroform.”*

\*or DOP

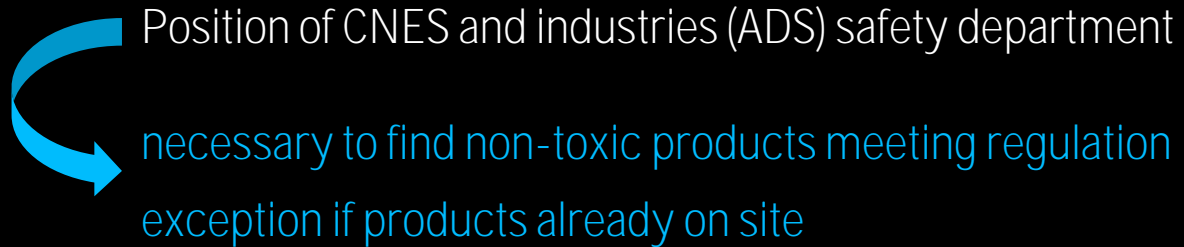
## MOTIVATION

health authorities and REACh: increasingly drastic regarding the use of such products

ECSS-Q-70-01C ⇨ ECSS-Q-ST-70-05C, Rev. 1 (2019)

Annex I (informative) : REACh exemption for DOP *for laboratory use of the substance in minute quantities*

But other uses: in larger quantities



## PREVIOUS STUDY

regarding only chloroform (ADS/CNES internship): starting point

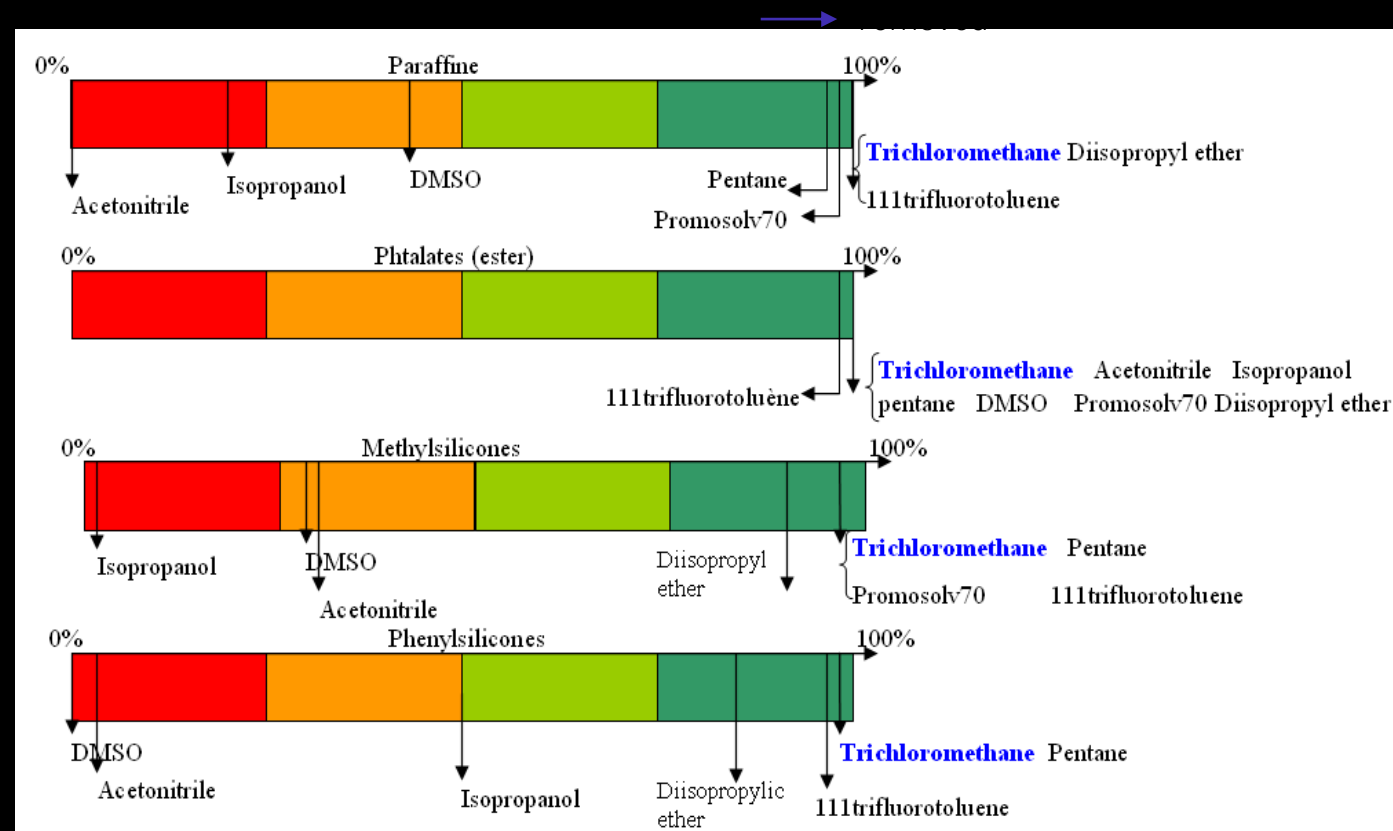
1. Definition of a list of potential alternative solvents
2. Study of the impact of those solvents on different substrates and efficacy in solubilizing contaminants
3. Real case analysis (deposit of outgassed species)

*promising results with 3 solvent candidates:*

- *n-pentane,*
- *1,1,1-trifluorotoluene*
- *Promosolv 70*

...Opportunity of green solvent

*Conclusion: carry out a formal qualification campaign following the preliminary study to validate the relevance of replacing chloroform for contamination analyses*



## RECENT STUDY

initial objective to find alternatives to the CMR products currently used:

➤ **alternative to chloroform**

a very powerful solvent, but also very dangerous

currently used as a solvent to clean contamination witness plates and solubilize all types of molecules including the 4 families of contaminants of interest (hydrocarbons, esters, dimethyl-silicones, phenyl-silicones) in ECSS-Q-ST-70-05C

3 uses of chloroform:

- ✓ analysis of contamination witnesses by indirect method (wipes)
- ✓ cleaning of witness plates
- ✓ cleaning of vacuum facility when contaminated by silicones

➤ **alternative to DOP used for the calibration of the IR spectrometer**

infrequent use but very restrictive because CMR

## RECENT STUDY

### key steps

T<sub>0</sub>: Kick-off

T<sub>0</sub> to T<sub>0</sub> + 3 months: Specifications definition

- Identification of products currently used (solvents and others) and associated applications
- State of the art to identify all existing alternative solutions for different application cases
- Detailed test plan with test conditions and characterizations

T<sub>0</sub> + 3 to T<sub>0</sub> + 5 months: Supply of solvents and necessary materials

T<sub>0</sub> + 5 to T<sub>0</sub> + 10 months:

- Tests campaign
- Characterizations and comparison of solutions

T<sub>0</sub> +10 to T<sub>0</sub> + 12 months:

- Results analysis and interpretation
- Evaluation of performances

## CHLOROFORM ALTERNATIVE

*analysis of contamination witnesses by indirect method (wipes)*

requirements

1. Be non carcinogenic, mutagenic, reprotoxic, or highly toxic.

Note: risk that the replacement solvent itself will be impacted by REACh or another type of restriction in future to be minimized

2. Have a non-volatile residue (NVR) less than or equal to 5 µg/g

3. Have no absorption bands in the same spectral range of the spectra of the four families of critical contaminants for space applications

4. Be able to solubilize the four families

5. Do not damage the contaminated surface

6. Evaporate quite quickly at room temperature



## CHLOROFORM ALTERNATIVE

*analysis of contamination witnesses by indirect method (wipes)*

3 research axes for replacement

- Internal (ADS different sites)
- From previous internship
- Literature

- REACH compliant
- Boiling point
- Vapor pressure
- Safety issues

*Others :*

*ionic liquids*

*substances from other fields of activity (e.g. pharmaceutical)*

solvents
<del>Diméthoxyethane</del>
<del>Cyclohexane</del>
Acétate d'éthyle
<del>Chlorure de méthylène</del>
<del>N-pentane</del>
Promosolv 70
$\alpha,\alpha,\alpha$ -Trifluorotoluène
<del>Lactate d'éthyle</del>
<del>1-méthoxy-2-propanol</del>
Promosolv Neo B1

4 selected solvents for NVR characterization and solubilization tests

	Residus	Hydrocarbons	Esters	Methylsilicone	Phenylsilicone	CMR	Safety status	PPE	Volume
Chloroform	0,0001 UA 0,001 µg.g <sup>-1</sup>	100,00 %	99,72 %	100,00 %	100,00 %	yes	RED	gloves, mask, glasses, blouse, hood	1 L
Trifluoro toluene	0,04 UA 0,29 µg.g <sup>-1</sup>	99,77 %	99,66 %	99,97 %	99,93 %	no	RED	gloves, glasses, blouse, hood	1 L
P 70	0,0045 UA 0,041 µg.g <sup>-1</sup>	98,97 %	99,08 %	100,00 %	99,91 %	no	Yellow/Green	gloves, mask, glasses, blouse, hood	30 L
P NEO B1	0,167 UA 1,79 µg.g <sup>-1</sup>	too high residus				no	Yellow/Green	gloves, glasses, blouse, hood	30 L
Ethyl acetate		too low volatility				no	Yellow/Green	gloves, glasses, blouse, hood	1 L

Good results for solubilization

but non compliant to ECSS specifications (NVR < 5 µg.g<sup>-1</sup> and absorbance level < 0,0001 AU unit)

## CHLOROFORM ALTERNATIVE

### *Cleaning of witness plates*

#### Preparation

- Preliminary contamination with mixture of methylsilicone and ester
- Cleaning with current protocole
- Solvent rinsing / UV-ozone cleaning

#### Tests

- Without rinsing
- IPA rinsing
- Trifluorotoluene rinsing

At that time: REACh compliant

But in the future ? PFAS (per/poly-fluoroalkyl substances) regulation ??


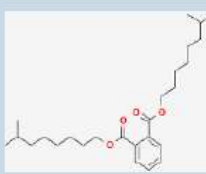
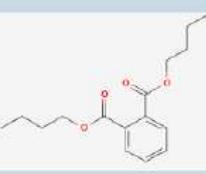
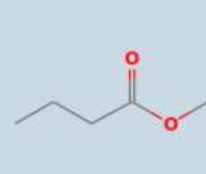
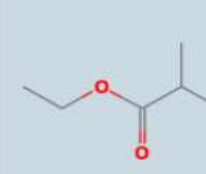
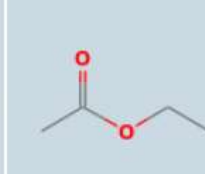








## DOP ALTERNATIVE

CMR/environmental issues

Ester absorption band similar to current one (1735  $\text{cm}^{-1}$ )

Note: Lessons learnt in cleanroom : 1721  $\text{cm}^{-1}$

Tested and selected

Name	DOP	Diisononyl phthalate	Dibutyl phthalate	Methyl butanoate	Ethyl propionate	Ethyl acetate	Ethyl benzoate
Formula							
$\nu_{\text{C=O}}$ ( $\text{cm}^{-1}$ )	1735	1728	1722	1742/1754	1752	Large 1755 (1752)	1726
Kept for study	 CMR	 CMR	 CMR	 Too high $\nu$	 Too high $\nu$	 Too high $\nu$	

## SUMMARY

- ECSS-Q-ST-70-05C indirect method (wipes)  
no alternative solution to chloroform – non compliant with the ECSS-Q-ST-70-05C requirements
- witness plates cleaning  
efficacy of trifluorotoluene  
60% reduction in chloroform consumption in the laboratory
- cleaning of silicones in vacuum facilities  
to be continued
- DOP alternative for spectrophotometer calibration  
ethyl benzoate may be identified



Finding alternatives is not trivial !

# CONCLUSION

Communicate, exchange

Anticipate

Traceability of materials and processes

Work together: studies, common approach, requirements revision?

# THANKS FOR YOUR ATTENTION ANY QUESTION?

