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INOVYN Contribution to Consultation on Medium Chain Chlorinated Paraffins (MCCPs)

INOVYN Chlorvinyls thanks the agency for the opportunity to contribute to this call for evidence.

INOVYN Chlorvinyls, previously INEOS Chlorvinyls, has been the lead registrant of MCCPs since the first registration deadline and remains active in that role. INOVYN is Europe's largest MCCP producer and has recently submitted grandfathering nominations for MCCPs under the UK REACH regulation and chairs the REACH consortium of registrants of MCCPs and is also chair of the Chloro Alkane Product Group (CAPG) which is part of the Eurochlor trade association. As such we have also been part of the discussions which have developed contributions from these two groups but also would very much like to ensure that INOVYN's own contribution is recorded.

We have divided the contribution into the following sections:

1. Production of Medium Chain Chlorinated Paraffins (Medium Chain Chloroalkanes) by INOVYN Chlorvinyls Limited
2. Biodegradation and Bioaccumulation
3. Demonstration of Safe Use
4. EU Sales and the relationship between chlorination level and application
5. The technical reasons for use of different levels of chlorination
6. Chlorinated Paraffins/alkanes globally
7. Carbon footprints of MCCP as a PVC plasticiser
8. Potential MCCP Alternatives
9. Summary

1. Production of Medium Chain Chlorinated Paraffins (Medium Chain Chloroalkanes) by INOVYN Chlorvinyls Limited

INOVYN Chlorvinyls has produced Medium Chain Chlorinated Paraffins (MCCPs, CAS 85535-85-9; EINECS 287-477-0) under the CERECLOR trade name for many years and took on the REACH lead registrant role in 2008 and has been the lead registrant since, registering the dossier in 2010 and updating it in 2014, 2017, 2018 and 2019. We are currently working on a fifth update to cover both the BREXIT process (since the EU REACH registrations have now been transferred to an EU legal entity) and to incorporate new data and a new bioaccumulation review.

At the heart of the subject is the fact that MCCPs are complex substances and are registered as a UVCB substance. Whilst a simple chlorination of ethane will yield chloroethane as a mono-constituent substance, as the carbon chain length of the alkane is increased the formation of structural isomers becomes significant and by the time the length of C_{14} to C_{17} is reached, numerous structural isomers are possible and, indeed, are formed. Tomy (1) calculated that the number of potential isomers for Short Chain Chlorinated Paraffins (SCCPs: CAS 85535-84-8) to be 6304: for MCCPs it will be in excess of 10,000. The chlorination reaction has generally low specificity, but the reaction sequence is generally:

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(i) Chlorination of one carbon atom at random, with formation of HCl, i.e.

$$C_{14}H_{30} + Cl_2 \longrightarrow C_{14}H_{29}Cl + HCl$$

(ii) Chlorination of a second carbon atom. This is likely to be some distance from the site of the first chlorination:

$$C_{14}H_{29}Cl + Cl_2 \longrightarrow C_{14}H_{28}Cl_2 + HCl$$

(iii) A third carbon atom is chlorinated, it will be as distant as possible from the first two sites:

$$C_{14}H_{28}Cl_2 + Cl_2 \longrightarrow C_{14}H_{27}Cl_3 + HCl$$

The process continues until adjacent carbon atoms along the chain are chlorinated, i.e. the formation of $C_{14}H_{24}Cl_6$. This is akin to the situation of single people gradually filling a train carriage: it is highly unlikely that people will sit adjacent to another person until it is necessary to do so.

Owing to the complexity of the overall product - and the fact that all these processes are taking place simultaneously - the final product yields tens of thousands of structural isomers. The inherently complex composition of each resulting product has always presented analytical challenges. Industry generally presents these products to the marketplace described by an average level of chlorination, e.g. 52% w/w. Products are analysed through reference to standards which have been subject to detailed analysis to determine their level of chlorination. General methods available to manufacturers in standard Quality Control laboratories are measurement of density, viscosity and refractive index, all of which show a linear relationship with chlorination with the range of chlorination levels of commercial products.

The relationship between % chlorination is given in detail in the registration dossier but, in summary, is given in Table 1 below. A similar relationship exists for $C_{15\text{-}17}$ alkanes.

The complexity has traditionally made analysis challenging. However as part of the REACH process the registrants have commissioned work with Vrij Universiteit in Amsterdam to develop new two-dimensional GC-MS methods and deconvolution of individual chlorination level (e.g. $-Cl_4$, $-Cl_5$, $-Cl_6$ etc.) is now possible although each peak still represents a large family of structural isomers of the same empirical formula. However, groups of isomers of the same carbon chain length and chlorination level can now be followed through biodegradation tests and the OECD 301D tests so performed show the faster degradation of the less chlorinated isomers. These are detailed in the 2019 dossier and Chemical Safety Report. We acknowledge the attempts made in this proposal to include chloroalkane products which contain constituents in the $C_{14\text{-}17}$ range. This is particularly important since there are differences in the way chloroalkanes are manufactured within European and North America regions and those manufactured in Asia. In the latter, products are often sold on chlorination level alone rather than a combination of carbon chain length and chlorination. As a simple extrapolation, 50% chlorinated alkanes of $C_{10\text{-}20}$ will have physicochemical properties similar to a $C_{14\text{-}17}$ MCCP at the same level of chlorination but will contain lower and higher carbon chain length chloroalkanes.

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Structure	% Chlorination
$C_{14}H_{29}Cl$	15.3
$C_{14}H_{28}Cl_2$	26.6
$C_{14}H_{27}Cl_3$	35.3
$C_{14}H_{26}Cl_4$	**42.3**
$C_{14}H_{25}Cl_5$	**47.9**
$C_{14}H_{24}Cl_6$	**52.6**
$C_{14}H_{23}Cl_7$	**56.5**
$C_{14}H_{22}Cl_8$	**59.9**
$C_{14}H_{21}Cl_9$	62.8
$C_{14}H_{20}Cl_{10}$	65.4

TABLE 1: Empirical Formulae for C_{14} Chloroalkanes (chlorination range of commercial products highlighted and highest volume sales underlined)

In our facility, chloroalkanes are manufactured in a large, integrated chemical facility with the principle technology on site being the manufacture of sodium hydroxide (caustic soda), chlorine and hydrogen by the electrolysis of sodium chloride solutions. This is seen as an essential industry and recently cited as such since the chlorine so produced then can be used in the manufacture of sodium hypochlorite, an essential biocide for anti-bacterial and anti-viricidal formulations. The Runcorn site is designated as Critical National Infrastructure and that the products produced are essential to a number of critical UK industries e.g. water and power and its provision of hydrogen is key in the development of hydrogen as part of the green economy.

While production of hydrochloric acid is not restricted to the chloroalkane process, owing to the exceedingly hydrophobic properties of chloroalkanes, the separation of hydrochloric acid from chloroalkanes is extremely straightforward and efficient, producing an acid of exceedingly high purity and meeting the specification requirements for the European Pharmacopoeia (maximum free chlorine 1 ppm; maximum sulphates 5 ppm; maximum heavy metals 2 ppm). Such purity is generally not possible for other organic routes to hydrochloric acid.

2. Biodegradation and Bioaccumulation

Given the complexity of the compositions and the near impossibility of predicting the biodegradation and bioaccumulation properties of an individual product, the registrants' proposal

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has always been to assess ready biodegradation potential testing of the commercial substances rather than specifically synthesised model compounds which carry no commercial significance.

We would like to remind DEFRA of the extensive number of OECD 301D ready biodegradation tests on commercial products of specified chlorination level, and substances synthesised at the request of regulators, submitted as part of the REACH registration process. Although the registrants appealed against the initial CoRAP decision (which was based upon the relationship between carbon chain length and degree of chlorination and biodegradation and bioaccumulation), the registrants followed this line of thought until the end of 2019 and, despite misgivings outlined in the appeal, performed tests specified on individually synthesised single chain length chloroalkanes which were also UVCB substances. The expense of such testing for registrants was significant.

Included in the OECD 301D tests are data showing the degradability of MCCPs with lower (<50% w/w) levels of chlorination. However, there are multiple acceptable biodegradation Studies on MCCP test materials in the 30-51% Cl (by wt.) range that show either ready or inherently biodegradable results. These are data in the REACH dossier that meet the Annex XIII criteria for a not P conclusion.

Since the last dossier submission in 2019, MCCP registrants have engaged in further persistence testing and have recently been involved in the test of a chlorinated paraffin in an OECD 314B test (Simulation tests to assess the biodegradability of chemicals discharged in wastewater). This showed nearly 90% biodegradability in just seven days in wastewater treatment plant sludges and, like the OECD 301D test data described above, shows the inherent potential of these substances for degradation. This study will be reported in the next update of the registration dossier and such data support a not P and therefore not SVHC conclusion.

Moreover, a new review of bioaccumulation has also been carried out by the independent reviewer [redacted] on behalf of the registrants using a Bioaccumulation Assessment Tool (BAT). This concludes that the majority (>80%) of reliable lines of evidence assessed showed that MCCP was not bioaccumulative in aquatic environments. Both of these recent developments – the OECD314 testing and the BAT - demonstrate the overall complexity of the substance and the need for a full assessment of the properties of all commercial products and, importantly, imported articles containing other chloroalkanes as alternatives.

We kindly request that the agency takes time to assess this new information as part of this call for evidence.

3. Demonstration of Safe Use

We would like to remind DEFRA that recent REACH CoRAP assessments confirmed that the Chemical Safety Report concluded that safe use was demonstrated for each application. We use these exposure scenarios in our extended Safety Data Sheets for customers and such reference ensures that MCCPs are used safely in Europe and suggest that a better action would be the exchange of these safe use templates.

We note also that the DEFRA presentation of 23rd February showed a slide of a triangle referring to a hierarchy of chemical classifications running from a chemical with a risk characterisation ratio (RCR)

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<1 to POP characteristics at the top. Whilst EA feel that these chemicals meet the POP characteristics (and therefore need for listing in the Convention), they also noted that MCCP RCR was <1. This comes over as contradictory.

4. The technical reasons for use of different levels of chlorination

Even within one broad use category, such as use as a plasticiser, there is variation in the requested chlorination level. Polymers are typically either melt processed, with mixing and compounding and subsequent melting while moulding, or are moulded as liquid dispersions (plastisols) and then subsequently melted and fused. The latter has constraints of the viscosity of the liquid media, including the plasticiser mix, so a lower viscosity is generally preferred, meaning that a MCCP grade of lower chlorination is normally specified. The other requirement of plastisols is a particular rheology (i.e. Newtonian, pseudoplastic, dilatant), depending upon the application. The key feature is that MCCPs do not interfere with the normal rheology of the polymer in use. In the melt-processed case, since moulding take place in the melt, the constraint of plasticiser viscosity is not so strong and a higher chlorination level is tolerated, especially if the end product is to meet a fire retardance specification. However lower chlorination level, typically 45% w/w, is preferred for plastisol applications since the plastisol viscosity is lower.

5. Chlorinated Paraffins/alkanes globally

Recent efforts by European manufacturers to reach out to producers in other parts of the world have resulted in symposia in Brussels (2012), Beijing (2015) and Delhi (2018). Each of these meetings yielded useful information on global manufacturing patterns which aided the understanding we had gained through selling our products in these regions. Given the additional transport costs for European manufacturers to sell in, for example, China, sales are normally of products which can command a quality or consistency premium for the user.

There is significant use of less specified products in the Asian market. As previously mentioned, one particular product being “CP-52.” Our understanding of these products is that they are manufactured from very wide cut -by EU standards - alkanes such as a $C_{10\text{-}20}$ or even a $C_{5\text{-}25}$ alkane. Indeed, there is often no specification of carbon chain length on the Chinese market but only on chlorination level, an observation confirmed by Gluge (2). The fact that a $C_{10\text{-}20}$ chlor alkane and a $C_{5\text{-}25}$ alkane will tend to have physical properties similar to that of an MCCP makes them useable, but we would question the end product properties if made from such material and the use of CP-52 in compounds may explain the observation of isomers in the $C_{10\text{-}13}$ range in a variety of studies on imported consumer goods (for example see reference (3) but we also note several references in the EU’s RAPEX report (4) on analysis of imported articles). The tightly controlled $C_{14\text{-}17}$ feedstock ensures that the presence of isomers below C_{14} are controlled. We point out that Gluge (2) estimated the volumes of the Chinese market to be 1 050 000 t in 2013 of which 90% was CP-52 and that, although we are not party to any official figures, we suspect that such a figure is now an underestimation. It is also concluded that the EU has become a small production base for chlorinated paraffins compared to Asia.

On the subject of CP-52 we would like to stress that, for the reasons given above, references to CP-52 as an MCCP are regarded as incorrect. We feel is also necessary to record the fact that we had an

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exchange of correspondence with the authors of one paper on the partitioning of chlorinated paraffins to daphnia magna (5). This included a reference to one of our products, CERECLOR 42, as a mixture of short chain chlorinated paraffin and medium chain chlorinated paraffin when it is in fact a long chain chlorinated paraffin. Discussions revealed that the authors had used samples in excess of 30 years old and there is the possibility of sample contamination. We would question any significance to any association between recorded effects and chain length for this product since the quoted composition is incorrect. Following two industry seminars on the subject INOVYN has developed a series of new analytical standards for use in research laboratories.

6. Carbon footprints of MCCP as a PVC Plasticiser

Carbon footprint and life cycle assessment are not part of a standard REACH or POPs assessment dossier, such properties are of significance in making regulatory decisions.

An independent life-cycle analysis has been performed on the production of chloroalkanes from INOVYN's production process (6). This assessed the use of our MCCP in the production of PVC articles are concluded that, compared to other PVC-related products, CERECLOR (the trade name for INOVYN chloroalkane products) has 28-45% lower carbon footprint impact than the other ingredients of the product. This is an important value in considering life cycle analyses of, for example, construction products.

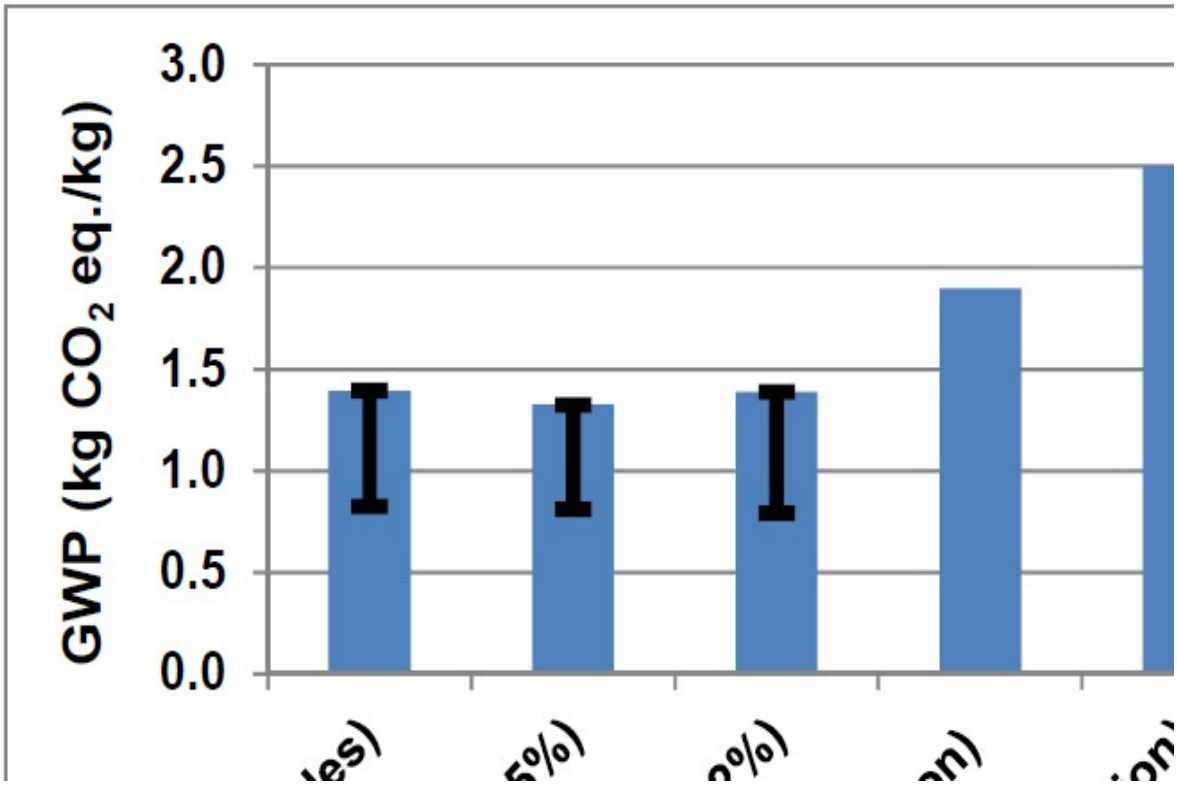

Fig. 1: Carbon footprint of CERECLOR compared to other PVC-related products

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[The upper error bar values (as well as the main bar) represent impacts after crediting the system for HCl production using the EU production mix; the lower error bar values represent impacts after crediting the system for HCl produced by hydrogen-chlorine synthesis].

7. Potential MCCP Alternatives

With the possible exception of long chain chloroalkanes (registered under REACH as paraffin waxes and hydrocarbon waxes, chloro (CAS 63449-39-8; EINECS 264-150-0) as a company we do not manufacture potential alternatives. Although long chain chloroalkanes may be seen as structurally similar, for several applications the higher chain length renders polymer incompatibility issues at lower concentrations and have too high a viscosity for any liquid polymer system. It is clear that there is no universally acceptable alternative.

In the case of PVC, where MCCP is used as a secondary plasticiser, substitution by the primary plasticiser in use is potentially possible, although with the exception of phosphate esters this will bring about a lower fire performance of the resulting product. The range of available primary plasticisers was recently reviewed (7) but the most recent overall assessment of alternatives was made by the UK Environment Agency, as part of the substance evaluation process, in September 2019 (8).

8. Summary

MCCPs are complex substances, classed as UVCBs under REACH, with tens of thousands of potential structural isomers. The complexity makes analysis difficult, but this is improving. There is a significant database on the persistence and biodegradation properties of MCCP and a recent review of bioaccumulation showed that the majority of studies indicated MCCPs to not meet the threshold for bioaccumulation.

Today, the EU is a relatively small market for the manufacture of chlorinated paraffins. Asia dominates the global market and different products are manufactured from wide chain length distribution products which are not MCCPs but are imported into the EU present in imported articles. Any unilateral action on MCCPs as defined in the REACH registration dossier will not have an effect on such products.

INOVYN requests that DEFRA reflects on this submission and the submission of the EU REACH consortium which presents details of the current commercial situation for MCCPs in Europe.

We remain at your disposal for any further questions and thank you for considering our contribution.

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