DIOXIN PROBLEM IN RUSSIAN CHEMICAL INDISTRY

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Russian problems caused with technogenic formation of dioxins and dioxin-like compounds are similar to well known problems of other world but with evident delay on more than twenty years and in absent of any offical estimation for ecological safety. The present report considers Russian industrial sources of dioxins arising simultaneously with mass production and treatment of some chemicals. The other members of former Soviet Union will be mentioned in case of need and mainly in connection with product shifts between plants.

Russian plants of mass chlorine products, including pesticides, turned out to be the most powerful dioxin sources.

In Chapaevsk (Samara province, former Kuibyshev) at the Plant of chemical fertilizers the appearance of dioxins mainly caused to the treatment of low toxic Cl_6-cyclohexan isomers:

Cl_6-cyclohexan --➤ Cl_3-chlorobenzene --➤
--➤ [Cl_4benzene] --➤ Cl_6benzene --➤ Cl_5-phenol.

The production of 1,2,4,5-Cl_4chlorobenzene from Cl_3-benzene was not success but accompanied with formation of the large amount of dioxins and evident morbidity enhancement of employees. Rest above stages also were the powerful dioxin sources. So in 1967-1981 dehydrochlorination of Cl_6-cyclohexan mixture was realized by pyrolisis at 240-260°, and transformation of Cl_3-benzene to Cl_6-benzene - by gas phase chlorination at 500-600°. After 1981 dehydrochlorination of Cl_6-cyclohexans were fulfiled by water alkali at 170-185°. The hydrolysis of Cl_6-benzene in alcogol at 150° was conducted only at first time and after the plant turned to hydrolysis in water alkali at $t^o > 230^o$. All processes were realized on unhermetic equipments, with a lot of hand operations and thus were accompanied with dioxin affectation of many hundreds employees. The sign of process dungerous - concentrations of PCDD in the the ending product PCP-Na were (data of 1990):

2,3,7,8-TCDD - 83.3 ppb;
sum of PnCDD - 46.7 ppb;
sum of HxCDD - 183.3 ppb.

In spite of this during many years the product was delivered to wood industry plants for timber preserving.

Partly Cl_3-benzene (mainly 1,2,4-Cl_3) was treated into Cl_6-benzene in Chapaevsk, and the rest was delivered to plant "Kra-

sitel" (Rubejnoe, Ukraine) for production of synthetic dyes and to transformer plant (Chirchik, Uzbekistan). The data about PCDD and PCDF contents are absent.

In Ufa at plant "Chimprom" the dioxin formation was caused with production of many chemicals.

The powerful appearance of dioxins was caused with industrial production of Bu-ether of 2,4,5-T (1965-1967). The mass exposure of employees with 2,3,7,8-TCDD was induced with dungerous for human conditions of hydrolysis of 1,2,4,5-Cl_4-benzene in water methanol (t^o of process 220-230^o). The additional amounts of TCDD were generated due to predioxin in the procedure of residual Cl_3-phenol distillation from acid 2,4,5-T at 220-230^o. The hermeticity of the operation was not provided. Nowdays that section produces another chemicals, but the administration did not admit the dioxin origin of employees exposure up to 1991 and the section proper was never cleaned from dioxins. Moreover other derivatives of 2,4,5-T (not Bu-ether) were produced at this plant some years after 1968.

Simultaneously the production 2,4,5-TCP was begun in Ufa (1963) in another section and continued up to 1988. At the same time this section produced 2,4,5-TCP Cu-salt. The section was not cleaned from dioxins after stoppage of production. At stoppage moment the 2,3,7,8-TCDD content in products was: in 2,4,5-TCP - from 1 to 30 ppm, in 2,4,5-TCP Cu-salt - from 2,2 to 2,8 ppm.

Further ways of these products were various enough. The 2,4,5-TCP Cu-salt was sent to the plant "Chimprom" (Pervomaiskii, Ukraine), and then after transformation to pesticides of phenthiuramic group went to rural regions. The 2,4,5-TCP was used more widely: partly it was transformated at plant"Krasitel" (Rubejnoe) to hexachlorophen for manufacture of antibacterial materials. During this production contamination sharply increased because of predioxin transformation to 2,3,7,8-TCDD (concentration 2,3,7,8-TCDD in final product was from 0.9 to 102 ppm on the moment of stoppage in 1988, depending on batch). The other part of 2,4,5-TCP was consumed by the experimental factory of Institute of chemicals for plants protection (Shchelkovo, Moscow province) for transformation to the pesticide threechlorometaphos-3. The rest product was consumed by the tunning industry.

From 60-ths up to nowdays the large amount of dioxins forms in Ufa during the production and purification of pesticides of group 2,4-D. Many technologic peculiarities of the process promote this. So the chlorination of phenol proceeded at 180^o, and the separation of chlorinated mass is not fulfil. The condensation of 2,4-Cl_2-phenol with monochloroacetic acid goes in alcalic conditions at 100-110^o (the filtration method) or at 130-160^o (the extraction method). The Cl_4-ethylene is used for purification in the extraction method of aminic salt 2,4-D obtaining. The proper extraction is realized at $t^o > 100^o$. The Cl_4-ethylene purification before repeated use is carrying out with water alkali at 130-140^o. The extraction of impurities

from raw 2,4-TCP solution in Cl_4-ethylene is executed with alcali solution. The formation of the PCDD and PCDF mixture in this process was never seriously discussed and there are no any reliable data about these PCDD and PCDF content in intermidiate products and commercial formulations.

Significant dioxin amounts are also arising in other Ufa productions (chlorobenzenes, hexachlorobutadien, Cl_3- and Cl_4-ethylenes etc.). The Ufa's production of pesticide aphalone (herbicide 326), which is accompanied with chlorinated azo- and azoxybenzenes besides conventional PCDD and PCDF, was copmletely prepared in the technological aspect in 1985 but was never beginning because of well known events in USA.

The formation of dioxins are unavoidable for many other chlorine technologies of Russian chemical industry, abundant with processes realized at high temperatures and pressures and at the alkalic conditions.

So the checking of dioxin content in propanide (propanyl) produced by plant "Syntesis" (Dzerdzhinsk), showed shortly before production stoppage some time ago that the product had contained even unexpected 2,3,7,8-TCDD in the concentration 6 ppb. The presence of related azo- and azoxybenzenes, including those arising during transformations of propanide after introduction of this pesticide to soil, was not discussed.

However the serious dioxin control of Russian chemical industry was not yet carrying on. So there are no data concerning to epichlorohydrin, producting on the plants "Caustic" (Sterlitamak) and "Chimprom" (Zima, Irkutsk province), about PCDD and PCDF impurities though accordingly to current technology one can confidently suppose their presence in significant amounts. There was not also carried out the detailed control of vinyl chloride produced on plants "Caustik" (Sterlitamak), "Chimprom" (Zima), "Caprolactam" (Dzerdzhinsk) and others by gas phase dehydrochlorination of 1,2-dichloroethane at high temperatures (400-550°).

The same concerns to Cl_3-ethylene - mass product, which is obtaining by alkali dehydrochlorination in liquid from 1,1,2,2-tetrachloroethane on plants "Kaustik" (Sterlitamak), "Chimprom" (Volgograd, Ufa and Usolje-Sibirian) and "Caprolactam" (Dzerdzhinsk), and is using in radio electronics for removing fat at high temperatures in alkali conditions. The distillation and rectification of raw Cl_3-ethylene are realized on chemical plants at 90-120° without analysis of PCDD and PCDF contents in still bottoms. The still bottoms of plants Volgograd (trade mark of the formulation is "Ritm"), Dzerdzhinsk etc. do not withdraw from circulation but are offering for sale as detergents.

Among bromoorganic compounds it may marked decabromodiphenyloxide used as antipyrene for plasticating of plastics. Recently it began produced at the plant "Altaichimprom" (Slavgorod). There are no data about PBDF impurities in this compound and especially about formation such impurities after antipyrene introduction into plastics.

PCB were produced in Russia during some ten years up to 1989-1990 mainly at plant "Orgsteklo" (Dzerdzhinsk) and in the lesser part at plant "Orgsynthesis" (Novomoskovsk, Tula province). During all post-war years PCN are produced mainly at plant "Chimprom" (Usolje-Sibirian). The hexachlorobutadien is produced in Ufa. The main purpose of this productions is to provide thr electrical industry.

The production of transformers and capasitors with different fillers: Sovol (PCB), Sovtol (mixture PCB with Cl_3-benzene) and Hexol (mixture PCB with hexachlorobutadien) - falls on several years, but mass production began at 60-ths and continued up to 1989-1990. In general for these purposes were spent from 300 to 500 ton PCB mainly produced on plants of Dzerzhinsk and Novomoskovsk, and also imported. The Cl_3-benzene had been received from Chapaevsk and in the lesser degree from other plants. The measurement of PCDF impurities in home and imported PCB was not done.

The filling of capacitors and transformers was executed on capacitor plants of Serpuchov (Russia), Ust-Kamenogorsk (Kazachstan) and Kamairi (former Leninakan, Armenia) and on transformer plant of Tchirchik (Uzbekistan). It was prepared about 100 thousand transformers with Sovtol filler and each of 10 to 2500 kg and some metallurgical and machine-building plants have several handreds of powerful transformers. The amount of capacitors is still more, however any data about working electrical devices dislocations are absent even for great batchas of powerful transformers. The exhaust capacitors and transformers are not yet gathered in special dumps and are completely absent any data about explosions and fires with participation of those. It is only known that Kamairi capacitor plant was destroyed with Armenian earthquake at 1989 but nobody was woorried with the fortune of PCB depots.

Conclusions:

1. Many Russian technologies of production and treatment of chlorine and bromine matters are powerful sources generating dioxins and dioxin-like compounds which disperse all over the country.

2. Methodical control and registration of dioxin containing products is not fulfiled.

3. Modernization of working plants with a view of decreasing of dioxin formation degree does not carry on.