

# OTHER HALOGENATED POPs OF CONCERN

## PRODUCTION OF POLYCHLOROTERPENES IN THE USSR

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### Introduction

This is a short report on the historical survey on the production and use of chlorinated terpenes in the USSR. It is based on information from Soviet literature and from interviewing people who had been involved in production and development of these pesticides. The massive list of references is omitted in the abstract; it's available from the author.

### Chronological table for the history of Polychloroterpenes in the Soviet Union

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1935-1936	The first chloroterpenic insecticide - Chlorinated Turpentine developed in NILECT.
1941-1945	Chlorinated Turpentine, under names SK or SK-9 is widely used as anti-pediculosis impregnant for underwear and bedclothes in the Red Army.
1949-1952	NIUIF develops Chlorten, Hexatene and Chlorphene, highly chlorinated bornylchloride and camphene, with chlorine content 63 – 70%. The new products are as effective as DDT in a majority of tests, while chlorinated terpenes seem to be much cheaper.
1953-1959	CNILHI is involved into development of chlorinated terpenes
1953-1960	Wide testing and experimental application of different preparations of Soviet polychloroterpenes in laboratories and in the field
1955	The technology for chlorinated terpenes is developed. Chlorination proceeds without solvent. A catalyst of free-radical chlorination – is employed. The product is purified with a flow of hot air instead of base-wash.
1957	The first 408 tons of polychloropinene produced on Chapaevsk Plant, its planned production capacity is 4 thousand tons per year
1958, May 23 <sup>rd</sup>	The first reported case of poisoning as a result of application of polychloropinene on sugar beet fields. 6 female workers got poisoned, one of them was taken to the hospital in a critical condition
1961-1962	The first medical examination on Chapaevsk factory. It is found that working on the production of polychloropinene might be “not quite safe”
1962	Annual production exceeds 3 thousand tons
1962	The first GOST (State Standard) for polychloroterpenes is introduced in USSR
1964	Pilot production of Polychloropinene launched in Dzerzhinsk
1965-1969	Chapaevsk plant switched from polychloropinene to polychlorocamphene
1967	Mainstream production of 65% concentrate of polychloropinene launched in Dzerzhinsk. Its planned production capacity was 17 thousand tons per year (11.05 thousand tons of pure ingredient)
Late 1960-s – early 1970-s	Mass use of polychloropinene as insecticide in Ukraine led to a series of accidental and occupational poisonings. Several lethal cases of swallowing: by little kids; with a purpose of suicide; by mistake. A number of cases of mass poisonings of workers on

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	sugar beet fields as a result of violation of recommended application protocol.
1968	Polychloropinene is found to be more dangerous than it was believed before
	Polydophen (a mixture of polychlorocamphene and DDT) is recommended for experimental use on cotton fields in Azerbaijan and Middle Asian Republics
1969	Production of polychloropinene in Chapaevsk stopped. The total amount of PCP produced in Chapaevsk in 1957 – 1969 is 28 thousand tons of active ingredient.
1969	The new GOST(State standard) for polychloropinene is introduced
1969 – 1979	44 thousand tons of polydophene produced on Chapaevsk Plant
1971	The GOST for polychlorocamphene is introduced
1978, March	Restriction of Polydophene “as DDT-containing”
30 <sup>th</sup>	Restriction of Polychloropinene, 50% oil concentrate “due to high persistence in the environment and discontinuance of production”
1981	End of polychloropinene production in Dzerzhinsk. An estimated total production in Dzerzhinsk is 132 thousand tons of active ingredient.
09.11.1981	Production and use of Polychloropinene are banned on the territory of USSR
1986	Restriction of Polychlorocamphene
1987	Production of Polychlorocamphene in Chapaevsk stopped. The total amount of 41.5 thousand tons of active ingredient has been produced in 1965 – 1987.
13.03.1991	Ban of polychlorocamphene on the territory of USSR
2000	Up to 1000 tons of polychloroterpenes are stored on the territory of the former USSR. No monitoring for residual polychloroterpenes in environment or food.

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### *Chlorinated turpentine – “Preparat SK”*

The Laboratory for Sanitary and Chemical Defence was established in 1935 in Moscow. The prime purpose of the laboratory was to develop a method for protection of Soviet army against pediculosis. The main idea was impregnation of underwear and clothes with chemicals that would kill lice on all stages of development and protect individuals from newcomers.

The development of SK was based on the two assumptions:

1. Both turpentine and chlorine have some insecticidal properties
2. Chlorination of turpentine would also lead to better stability of impregnated material.

The chemical part of the job was done by a group of synthetic chemists under leadership of S.V. Zhuravlev. It is not clear, whether chlorination was stimulated by heating only or by irradiation or addition of a free-radical catalyst. A series of products were synthesized, with different content of chlorine (from 30 to 60 %), they were studied as “monochloroturpentine, dichloroturpentine,... Hexachloroturpentine”. The minimal content of chlorine for practical use was determined as 50 %, and 58-60 % was found to be the best; this corresponds to around 5.5 chlorine atoms in a molecule. Therefore SK might have contained significant amounts of hepta- and hexachloroterpenes. SK was used as emulsion, as dust and as an ointment against pediculosis during WWII. Later on it has had mainly veterinary application as acaricide against Ixodes on cattle; till about 1980. It was used under different names – SK, SK-9, Antipediculin SK, SK-34, SK-47.

There are no data on when, where, how and in what amounts it has been manufactured.

An estimation of its use during the WWII is not more than 2.5 thousand tons.

### *Other developments of chlorinated terpenes*

Chlorten and Hexaten were the nicknames for the first developments of NIUIF (Scientific Institute for Fertilizers and Insecto-Fungicides). Chlorten is a product of chlorination under UV-light of

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bornylchloride in carbon tetrachloride solution, while Hexaten – in benzene solution. Thus Hexaten is a mixture of chlorten with HCH.

Chlorphen was synthesized in the same manner from camphene.

Polydophen was a commercially produced mixture (1968-1979, amount of polychlorocamphene involved – 17.5 thousand tons; applied on cotton in Uzbekistan, Tadjikistan, Turkmenistan, Kirgizstan and Azerbaijan) of polychlorocamphene and DDT in the ratio 2:1. The similar mixtures of chlorten and chlorphen with DDT have been prepared and tested in the 50-s as well.

Chlorpinak (chlorinated pinene – insecto-acaricide) is a product of direct chlorination of pinene, with chlorine content 66-67%. In Russian literature it is considered as identical to Strobane. It was not produced commercially.

In about 1960 Bardyshev developed a method for preparation of “emulsified chlorten”, a product of chlorination of mixtures of pinene, camphene and colophony. The product was ready-to-use for preparation of emulsions and did not require an addition of an emulsifier. However, this was not produced commercially.

A patent for preparation of polychlorodipentene with 73-80 % of chlorine content appeared in 1967 by chlorination of “Dimer fraction” – a by-product of polyisoprene rubber. Another patent (also 1967) describes polychlorobornylene. Neither one was produced commercially.

### *Total production of chloroterpenes in the USSR*

The total amount of chlorinated terpenes, produced in the USSR is not more than 210 thousand tons (including hypothetical 8.5 thousand tons of Preparat SK, produced in 1940 –1980).

### *Polychlorocamphene and Polychloropinene - Technology*

These two were main chloroterpene insecticides. In USSR a terpene was chlorinated without solvent, and the product was purified from HCL and other volatile compounds by passing hot air through it, instead of being base-washed.

### *Composition of Polychloropinene and Polychlorocamphene – chemical consideration*

The main difference between pinene and camphene as starting materials is that pinene yields bornyl chloride in reaction with HCl almost quantitatively, via rearrangement. Therefore it is bornyl chloride, which undergoes further free-radical chlorination on the way to Polychloropinene.

Therefore Soviet polychloropinene probably does not contain polychlorodihydrocamphenes at all, and must be a mixture of polychlorobornanes, and possibly polychlorobornenes. What can be the difference in composition of polychlorobornanes in Soviet PCP and in Toxaphene?

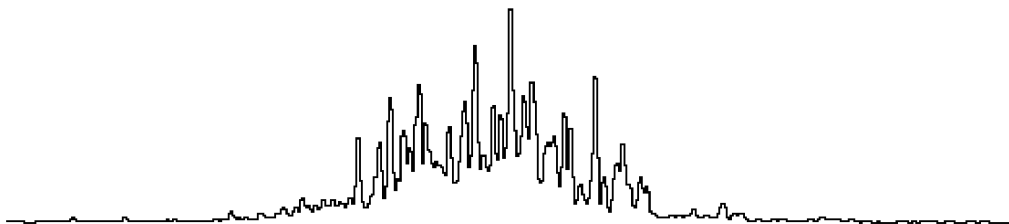
— All chlorobornanes (about 70) isolated so far from chlorination of camphene, contained at least one Cl at C-10, because the intermediates, 2-exo,10-Di- and 2-exo,10,10-trichlorobornanes both already have such atom in a molecule. This is not the case for Bornyl chloride (2-exo-chlorobornane). Therefore compounds with an unsubstituted methyl group at the bridgehead might be present in the Soviet polychloropinene.

— Soviet PCP should have lower percentage of compounds with two Cl atoms at C-10, because that would require double chlorinating of methyl group at the bridgehead (nothing required for the derivatives of 2,10,10-triCB, and just a single chlorinating for the derivatives of 2,10-DiCB). Therefore, content of the well-known environmentally relevant congeners, such as Parlar nos. 26, 40, 41, 44, 50 and 62 can be significantly lower in the Soviet Polychloropinene, compare to Toxaphene. Correspondingly, the share of USSR contribution into the global pollution can be smaller than its share in the gross production. On the other hand, different starting material might lead to higher content of one or several key congeners.

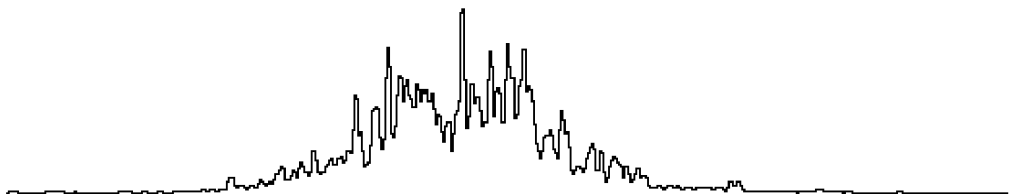
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*Chromatograms of Toxaphene (a), Polychlorocamphene (b) and Polychloropinene (c)*

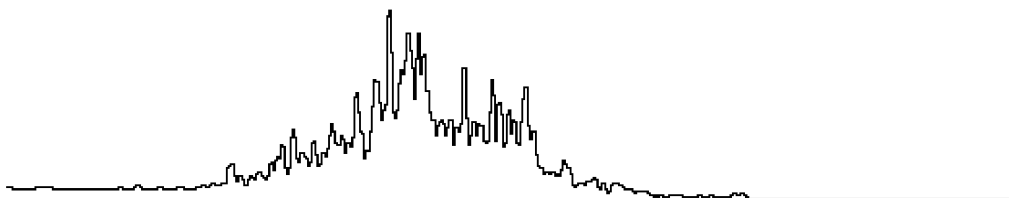
a)



b)



c)



## *Composition of Polychloropinene and Polychlorocamphene – Conclusions*

The following conclusions can be made regarding composition of Soviet polychloroterpenes :

1. Soviet polychloropinene and polychlorocamphene must contain a number of major components of Toxaphene in comparable amounts
2. Polychlorocamphene, Polychloropinene and Toxaphene have different GC-ECD patterns (therefore different composition), due to different technologies, despite similar content of chlorine
3. Polychloropinene is likely not to contain polychlorodihydrocamphenes
4. Polychloropinene from Dzerzhinsk and Polychloropinene from Chapaevsk differ significantly, by an average of 0.64 chlorine atom per molecule

## **Acknowledgements**

Author is grateful to all who provided information and to Hercules Inc. for support and inspiration.