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Review of the Six Generations of Red phosphorus 1950 –1999 and beyond

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Abstract

The performance and processing requirements for red phosphorus in pyrotechnical applications have change significantly over the last 40 years. Originally the US military community provided the definition for red amorphous phosphorus within the MIL-Spec. Whilst these specifications have been revised and updated, the existing performance and shelf life requirements have forced producers and processors to examine other red phosphorus options to meet the most exacting modern pyrotechnical requirements.
Clariant (formerly Hoechst, Knapsack) as the world's largest producer of red phosphorus has invested substantial resources in providing state of the art red phosphorus grades which have been specifically tailored to the exacting requirements within the military and civilian pyrotechnical industries.
The presentation will review the red phosphorus market and usage trends as perceived by Clariant, and will cover the chemical, physical and processing developments of the six generations of red phosphorus since 1950's, and will provide an insight into the direction in which red phosphorus could develop in the next millenium.

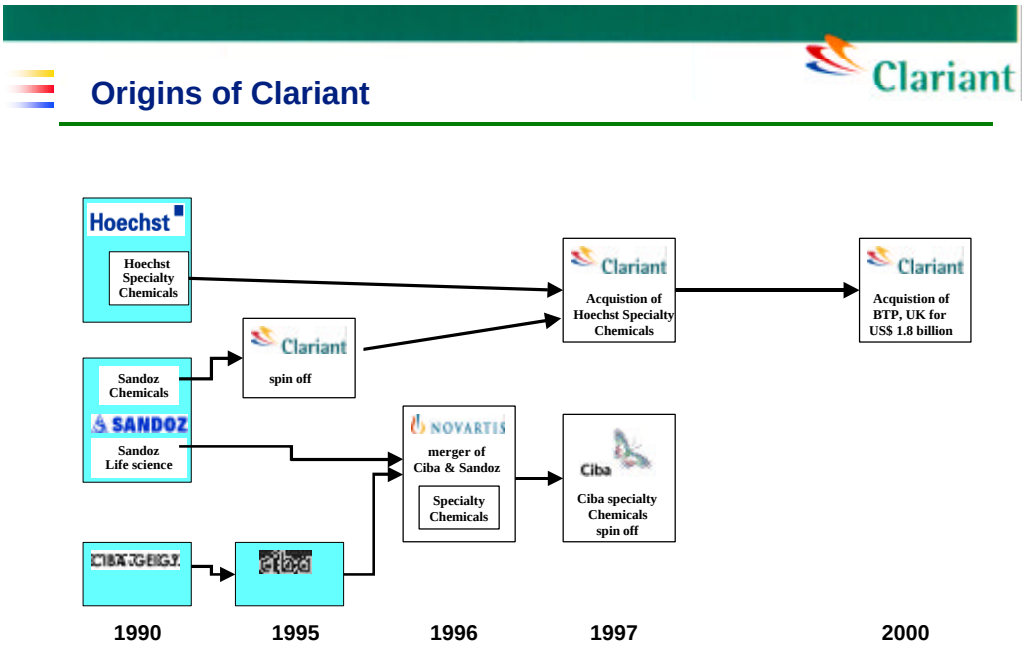
Introduction

Red Phosphorus has been produced continuously Knapsack since 1953. The production facility was originally constructed by Knapsack AG, which was subsequently acquired by Hoechst AG. In 1997 Clariant AG Switzerland bought Hoechst's Speciality Chemicals business. Clariant has continued to expand by acquiring BTP, UK to become a US$ 7 billion speciality chemicals company

Clariant has also continued to invest in the red phosphorus business, and purchased the remains of Albright & Wilson's red phosphorus business in late 1998, the activities and know-how have been integrated into Clariant's red phosphorus business in 1999.

Clariant specialises in the production of high specification red phosphorus based products which are designed to meet specific customer performance criteria.

We will now examine how these criteria have changed and been modified to meet the performance requirements expected of today's red phosphorus



Clariant is a US$ 6 billion company focussed on Specialty Chemicals

1st Generation Red phosphorus

The first generation of red phosphorus basically evolved after the Second World War in the late 1940's and early 1950's when the US military introduced a procurement specification for red phosphorus powder. The result was the initial version of US MIL-P-211. The focus was to try and control the presence of white phosphorus and moisture. These were key issues in the processing and stability as the white phosphorus is spontaneously combustible and the moisture content was used to ensure dry material was delivered.

- 1950 - 1970's
  - initial MIL-P specifications by US military
  - use of unstabilised red phosphorus powder
  - differentiation by moisture & purity (RP/ WP)

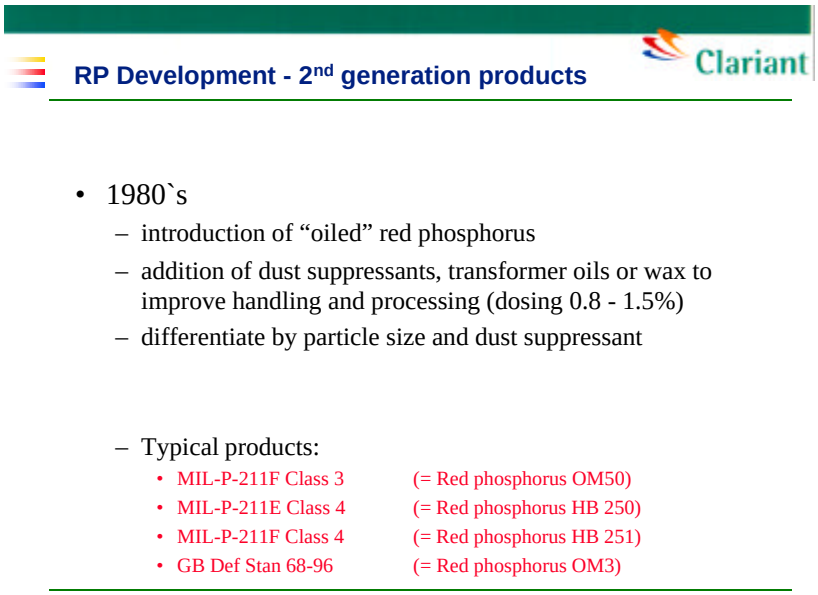
  - Typical products:
    - MIL-P-211F/ Class 1 (= Red phosphorus SF)
    - MIL-P-670A (= Red phosphorus HB 710)

2nd Generation Red phosphorus

The 1980's saw the introduction of "oiled" red phosphorus which basically involved the introduction of dust suppressants. The addition of dust suppressants had a two-fold effect:

- improved handling by reducing risk of dusting and consequent fires
- coating the surface of red phosphorus to reduce rate of oxidation

In practice the red phosphorus producers "oiled" the material and then the red phosphorus customers then used a solvent (e.g. acetone, methylene chloride) to strip off the oil before processing. The US MIL-P-211 specifications required 0.8 – 1.5% dust suppressant, and allowed the use of commercially available long chain ethoxylates rather than the original transformer oils.
An additional focus was give to the particle size distribution as it became apparent that this impacts the burn time and burn rate.

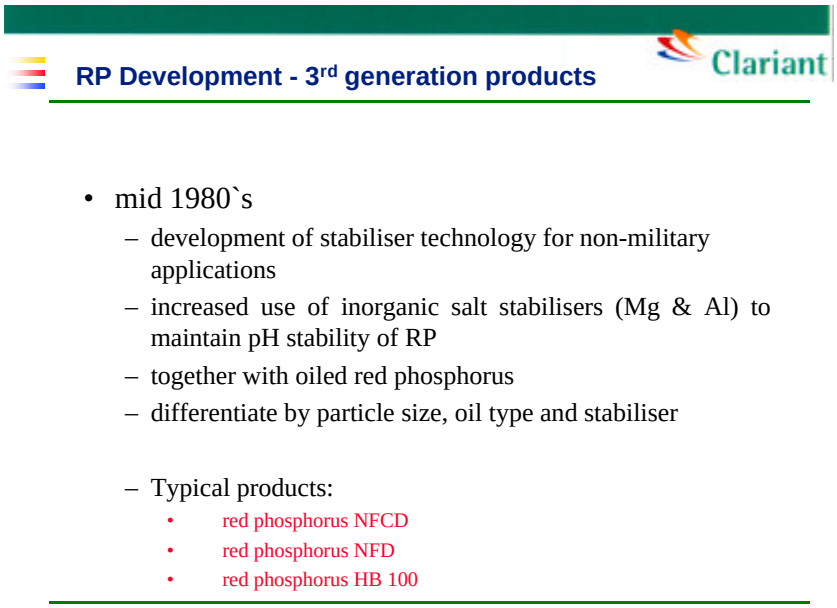


3rd Generation Red phosphorus

In the mid-1980's the stabiliser technology for red phosphorus improved further driven by the match making and plastics industry who were looking for increased

The basic idea can be found in the MIL-P-670A dating back to 1948 but this was mostly only used for Navy markers and not for smoke & obscurant applications. The MIL-P-670A included an aluminium stabiliser coupled with a basic particle size distribution requirement but no dust suppressant.

The new stabiliser development was combined with the dust suppressant & particle size distribution know-how to create an initial range of Red Phosphorus HB grades. The HB – range was developed through a close relationship with selected military sub-contractors who were flexible in their development programs.



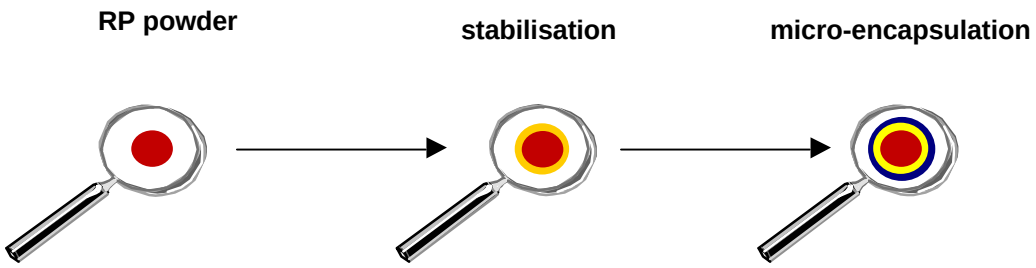
4th Generation Red phosphorus

The 1990's saw the development of a micro-encapsulation technology by Clariant to coat red phosphorus particles with a thin film of polymer. The introduction of micro-encapsulation for red phosphorus dramatically improved the stability and allowed red phosphorus powders to be introduced to the polymer industry as high performance flame retardants. These red phosphorus grades are sold under the Exolit RP brand name. However the major barrier for larger scale use was still the fact that the polymer industry did not wish to work with red phosphorus powder

The micro-encapsulation was combined with the stabiliser technology to introduce red phosphorus in new delivery forms to meet the customers processing requirements:

aqueous systems and dispersions
epoxy and resin system
dust suppressed ("oiled") powders

Generally speaking these developments were largely ignored by the pyrotechnical and military communities, and they were only used by a limited number of independent commercial contractors for new projects.



RP Development - 4th generation products

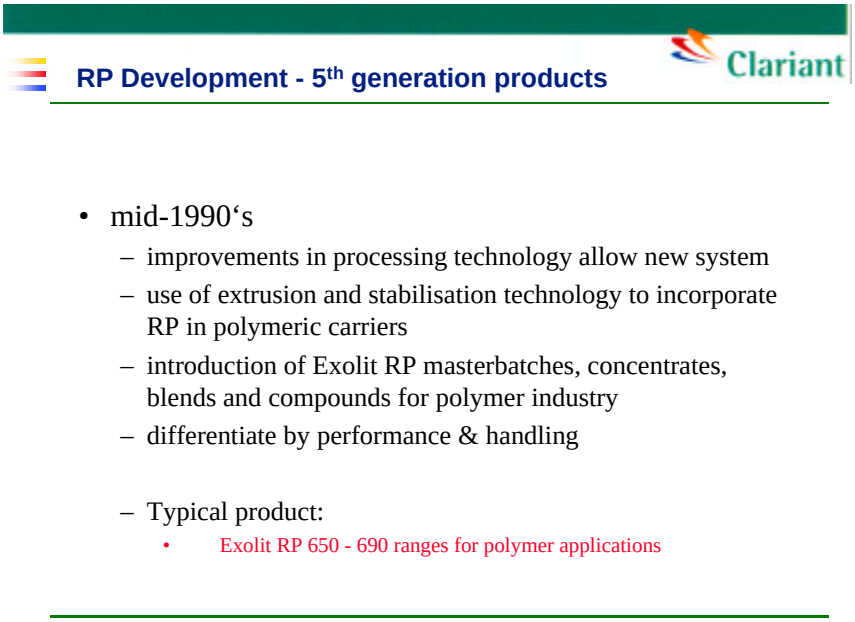
- early 1990's
  - development of RP microencapsulation by Clariant
  - use of micro-encapsulation technology to coat RP powders
  - continued use of inorganic salts stabilisers
  - allows production of aqueous systems and pastes
  - allows production of RP expoxy/adhesive systems
  - differentiate by particle size, coating, system and stability

  - Typical products:
    - red phosphorus HB 300 & HB 400
    - red phosphorus HB 600 & HB 700
    - red phosphorus HB 701 & HB 714

5th Generation Red phosphorus

The next step saw improvements in the processing technology which allowed extrusion of red phosphorus in polymeric carriers. Red phosphorus is now available in a wide range of polymer carriers like polyolefins, polyamides and special thermoplastic resins. The polymer industry is now able to obtain the red phosphorus as compounds or masterbatches which eliminates the issues of handling red phosphorus powders.

Since these breakthrough the polymer industry has become the major market for red phosphorus based products which function as high performance flame retardants. Accordingly the polymer industry is now driving the development efforts in the area of red phosphorus especially as red phosphorus has now become accepted as an environmentally friendly flame retardant.



6th Generation Red phosphorus

The development work is continuing driven by the requirement to further improve the phosphine stability and to produce flame retardants with better performance characteristics. The initial product, red phosphorus HB 800, is currently being patented and selective sampling is being carried out to evaluate its performance.

The future research and development work will continue to be focussed on the technical improvements required to further penetrate the polymer industry with high performance flame retardants.