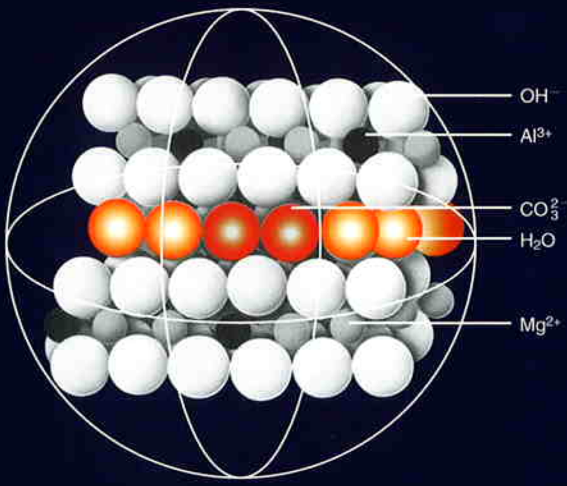
HALOGEN SCAVENGER



DHT-4A

Kyowa Chemical Industry Co., Ltd.
Kisuma Chemicals B. V.

KYOWA CHEMICAL INDUSTRY CO., LTD

KISUMA CHEMICALS

DHT-4A

[Hydrotalcite-like Compound]

Hydrotalcite [$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$] occurs naturally in small deposits in the Urals of the Russian Federation and also in Snarum, Norway. In 1966 **Kyowa Chemical Industry Co., Ltd.** succeeded in the world's first industrial synthesis of hydrotalcite. Initially our synthetic hydrotalcite found an application in the pharmaceutical industry as an antacid. This product has been marketed worldwide via several prominent pharmaceutical companies.

At a later stage hydrotalcite-like compounds were developed, specifically aiming at industrial polymer processing, in which halogen immobilization is required in this type of application full use can also be made of the unmatched acid neutralization features of hydrotalcites.

DHT-4A is a synthetic Hydrotalcite-like compound and has recently been developed for use as a stabilizer (halogen scavenger) in plastic processes such as the production of polyolefins.

DHT-4A is needed to produce polyolefins which have residual catalyst components.

DHT-4A is the most suitable halogen scavenger for transparent films of polyolefins because of its low level of water carry-over as well as its refractive index which is close to that of polyolefins.

DHT-4A is indispensable in producing adhesive graft polymers in which calcium stearate can not be used due to bleed-out.

DHT-4A provides long term weatherability when used with HALS.

Advantages of DHT-4A

DHT-4A reacts with and deactivates the residual quantities of acidic substances associated with Ziegler-Natta, Friedel Crafts, Metallocene or other acid catalysts used to produce polymers or elastomers. As a result DHT-4A can markedly reduce or eliminate corrosivity and improve the polymers heat resistance and weathering properties. DHT-4A is particularly useful in polypropylenes made with high-yield catalysts that have no need for a de-ashing process. However, the PP produced in this process contains a considerable amount of halogen residual catalyst components, for example approximately 10 to 300 ppm of Cl^-. Such concentrations may cause problems of corrosion in molding equipment or degradation of the polymers themselves. Ideally halogens of this nature should be rendered inert. Through a unique adsorptive characteristic DHT-4A is able to do just this.

The conventional agent used in this application is calcium stearate, but DHT-4A is superior for the following reasons:

(1) Quantities of additives are minimized.
 DHT-4A has about 5 times the capacity of calcium stearate to protect against corrosivity. Any loss of the polymers physical properties resulting from additives is thereby reduced.

(2) Polymer yellowing is avoided.
 When DHT-4A contacts phenolic type stabilizers such as B.H.T., that are widely used as antioxidants, DHT-4A does not cause polymer yellowing.

(3) No stearic acid vapor problem.
 By using DHT-4A, troublesome stearic acid vapors can be eliminated.

(4) Reduction of water carry-over.
 The amount of water carry-over while using DHT-4A is noticably less than in the case of calcium stearate.

Characteristics of DHT-4A

A unique mechanism of acid-adsorption

The superiority of DHT-4A is mainly due to its particular mechanism of adsorbing acids. DHT-4A has a substantial anion-exchange property. For example, in the case of HCl, CO_3^{2-} of DHT-4A is easily ion-exchanged by Cl^-, and accordingly, the chloride ion is adsorbed and fixed in a stable crystal structure.

$$Mg_{4.5}Al_2(OH)_{13}CO_3 \cdot 3.5H_2O + 2HCl \rightarrow Mg_{4.5}Al_2(OH)_{13}Cl_2 \cdot mH_2O + H_2O + CO_2$$

The resulting compound (Chloride type DHT) is insoluble in both water and oil. In addition, a temperature of approximately 450°C is required for Cl^- to be released from the structure. Though calcium stearate neutralizes acids such as HCl by forming $CaCl_2$ and stearic acid, the resulting $CaCl_2$ is hygroscopic and dissolves in water.

$$Ca(C_{17}H_{35}COO)_2 + 2HCl \rightarrow CaCl_2 + 2C_{17}H_{35}COOH$$

The stearic acid produced has the disadvantage of causing corrosion of molding devices and bleeding out on the surface of the molded product.

Surface-coated Fine Particle

DHT-4A has not only an ion-exchange property but also has excellent physical properties as a powder. DHT-4A consists of very fine particles synthesized by Kyowa's proprietary technique. These particles are treated with a surface active agent which enable them to have good affinity with polymers. Therefore high dispersibility is achieved.

The mean particle size is approximately 0.4μm (micrometer), so DHT-4A may be used even in ultra-thin films or fiber resins without altering the texture or appearance of the product.

Safety Information

The fact that Kyowa's hydrotalcite has been used as an antacid world-wide in the pharmaceutical industry is indicative of DHT-4A's health and safety status.

Since DHT-4A is insoluble in both water and oil, aqueous or oily foods may be packaged in films containing DHT-4A without the concern that DHT-4A will migrate into the food. Only in the case of acidic food is there a possibility of migration. In this case, very small quantities of magnesium and aluminum ions which are "GRAS"*, may be observed.

DHT-4A is registered as a positive material in polyolefin used for food packaging in many countries.

*"GRAS": *Generally Recognized As Safe substance for food additive by FDA in the U.S.A.*

Registration

CAS No.	11097-59-9
Food contact materials (EU)	PM/REF No.34690
FDA	Equivalent product to GRAS
* Food contacting package (Japan)	Registered

* Compliance with The Self-Restrictive Standards for Food-Contacting Package-Container and Utensil Made of Polyolefins and Certain Polymers (Japan)

Recommended Ratio of Additive to Mix

The following represents a typical quantity of DHT-4A required in the production of PP. In the case where high yield catalysts are employed and the usual de-ashing process is eliminated, from 0.001 to 0.3 parts by weight of DHT-4A are required together with other additives to 100 parts by weight of dry PP powder. The mixture is then kneaded, and pelletized by an extruder.

The dosage of DHT-4A is about 10 to 20 times the residual Cl in PP.

Standard Export Package

DHT-4A is packaged in a polyethylene bag or a 4-ply polyethylene/paper bag net wt. 20kg. The first inner ply is 0.10mm polyethylene and is sealed by heat. The remaining 3 plies are kraft paper sealed with cotton string stitching.

Properties of DHT-4A

Chemical Formula : $Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot mH_2O (0 < x \leqq 0.5)$

Chemical Description : Magnesium Aluminum Hydroxide Carbonate Hydrate

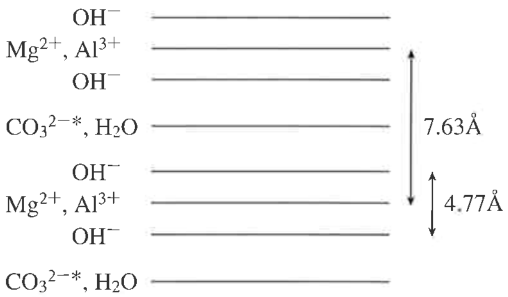
Product Appearance : A white, odorless, fine powder

	Typical Analysis
Magnesium as MgO	34%
Aluminum as Al_2O_3	19%
Molar Ratio of MgO/Al_2O_3	4.5
Loss on Drying *(at 105°C for 1 hour)*	0.34%
Heavy Metals.	10 ppm max.
Specific Surface Area *(BET method)*	11m^2/g
pH of Suspension *(1g/50ml $C_2H_5OH+H_2O$) (1:1)*	8.55
Particle Size Distribution	under 1 μm: 85.0min. (vol %) over 5 μm: 0.0 (vol %) average (μm) : 0.30-0.60
Packed Volume *(standard packing)*	approx. 0.06m^3/20kg bag

TECHNICAL INFORMATION OF DHT-4A

1) Crystalographic Properties

Formula	: $Mg_{4.5}Al_2(OH)_{13}CO_3 \cdot 3.5H_2O$
Space Group	: $R\bar{3}M$
	a_o=3.048Å, c_o=22.90Å
Hardness (Mohs')	: 2.0-2.5
Density	: 2.1
Refractive Index	: 1.49-1.51 (Birefringence)
Crystal Structure	: Layer Sequences are as follows:



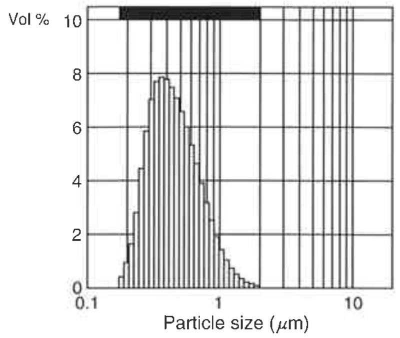
CO_3^{2-} can be ion-exchanged by another anion, such as Cl^-, F^-, NO_3^-, SO_3^{2-}.

2) Instrumental Analysis

(2-1) X-ray Powder Diffraction

d(Å)	I/I₀	hkℓ
11.8	1	002
7.5750	100	003
3.784	37	006
2.616	2	101
2.569	12	102
2.523	3	009
2.274	8	105
1.928	8	108
1.884	1	00, 12
1.720	2	10, 10
1.625	1	10, 11
1.522	6	110
1.492	6	113
1.455	1	10, 13
1.411	2	116
1.381	1	10, 14
1.309	1	202
1.264	1	205
1.249	1	10, 16

(2-2) Particle Size Distribution



The above histogram is defined by a laser scattering particle size distribution analyzer. (9320-×100 made by Nikkiso)

(2-3) Thermal Analysis by DTA and TGA

The interlayer water (approximately 12%) starts to dehydrate at approx. 180°C up to approx. 300°C. The crystal structure remains unchanged up to about 350°C. The crystal structure decomposes at approx. 350°C when the H_2O and CO_2 have evoluted from the structure, and a MgO-Al_2O_3 solid solution having the formula of $Mg_{1-3x/2}Al_xO$ is formed. This solid solution is stable up to 800°C. On further heating MgO and $MgAl_2O_4$ are formed at approx. 900°C. The original crystal structure of the solid calcined at less than 800°C can be restored by hydration.

Fig. 1 — DHT-4A [$Mg_{4.5}Al_2(OH)_{13}CO_3 \cdot 3.5H_2O$]

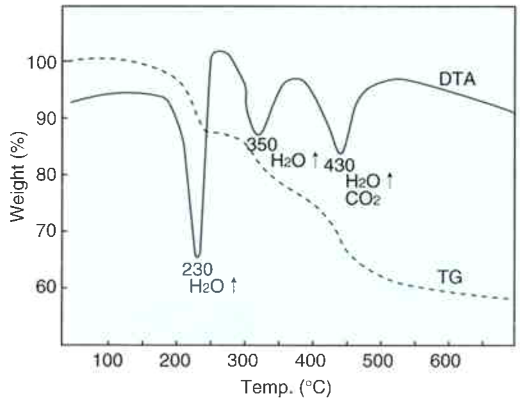
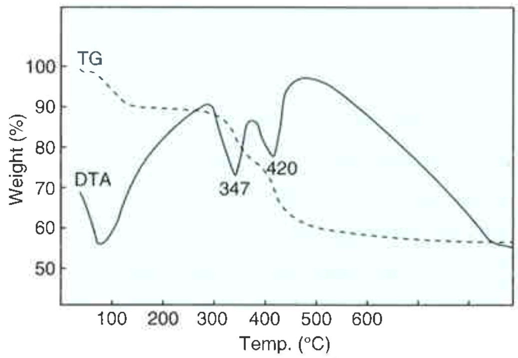
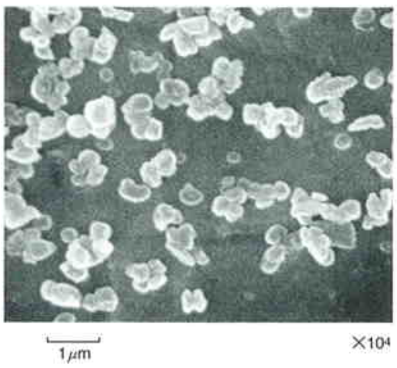


Fig. 2 — Chloride Type of DHT [$Mg_{4.5}Al_2(OH)_{13}Cl_2 \cdot mH_2O$]

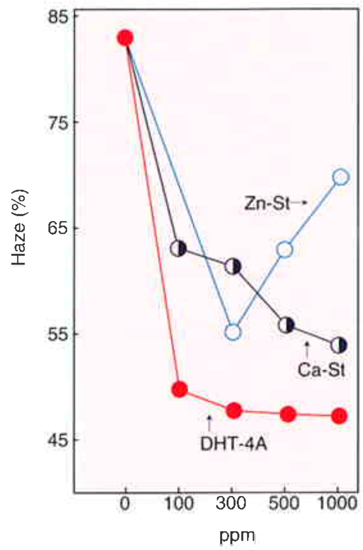


(2-4) Electron Micrograph

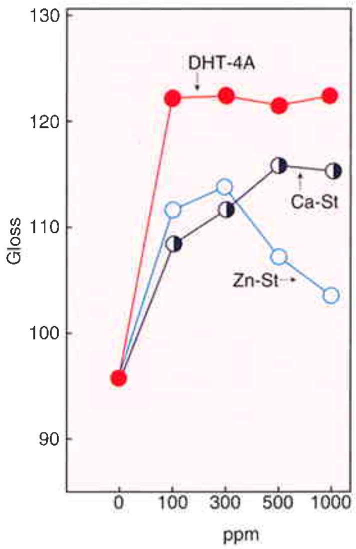


3) The effect of DHT-4A on a polymer

(3-1) Haze



(3-2) Gloss

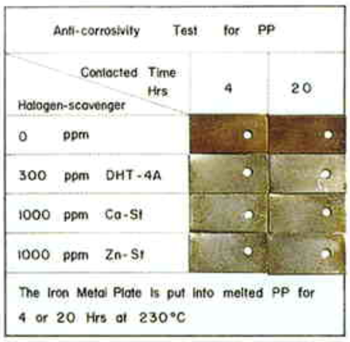


Formulation:

H-PP (Cl : 20ppm)	100phr
Halogen scavenger	varid ppm
Irganox 1010	500ppm
Irgafos 168	500ppm
DBS	3000ppm

Extruder : 230°C
Press : 230°C×3min
Thickness : 3mm

(3-3) Anticorrosion Test



Test method

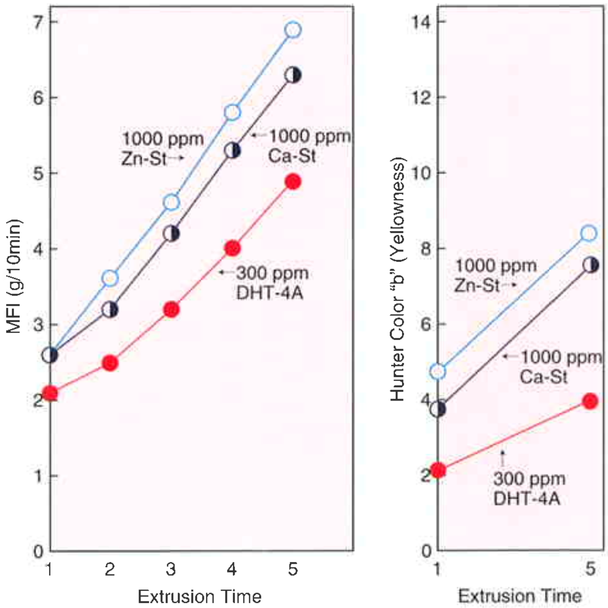
Two soft iron plates were put into PP pellets and placed in an oven at 230°C one plate for 4 hours and the other plate for 20 hours. The iron was then taken out and the residual PP was wiped off. It was then hung from the cap of a glass bottle (500ml) containing a small amount of water. Care was taken to ensure that the metal did not touch the water.

It was then kept at room temperature (around 20°C) for 7 days.

Composition of the iron plate

C	: 0.15%
Si	: 0.24~0.25%
Mn	: 0.95%
P	: 0.014%
S	: 0.015%
Fe	: The balance

(3-4) Processing Stability at 230°C



Formulation

PP	100phr
Halogen scavenger	varid ppm
Irganox 1010	500ppm
Irgafos P-EPQ	500ppm

The residual Cl in PP is approx. 30ppm

The data presented in this catalog are not guaranteed values. DHT-4 is an inorganic powder which serves as an easily handleable acid acceptor.

Testing is recommended first. Questions on any obscure points are welcome.

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