阻燃剂的阻燃原理详解

阻燃剂是通过若干机理发挥其阻燃作用的，如吸热作用、覆盖作用、抑制链反应、不燃气体的窒息作用等。多数阻燃剂是通过若干机理共同作用达到阻燃目的。

1、 吸热作用

任何燃烧在较短的时间所放出的热量是有限的，如果能在较短的时间吸收火源所放出的一部分热量，那么火焰温度就会降低，辐射到燃烧表面和作用于将已经气化的可燃分子裂解成自由基的热量就会减少，燃烧反应就会得到一定程度的抑制。在高温条件下，阻燃剂发生了强烈的吸热反应，吸收燃烧放出的部分热量，降低可燃物表面的温度，有效地抑制可燃性气体的生成，阻止燃烧的蔓延。$Al(OH)3$ 阻燃剂的阻燃机理就是通过提高聚合物的热容，使其在达到热分解温度前吸收更多的热量，从而提高其阻燃性能。这类阻燃剂充分发挥其结合水蒸汽时大量吸热的特性，提高其自身的阻燃能力。

2、 覆盖作用

在可燃材料中加入阻燃剂后，阻燃剂在高温下能形成玻璃状或稳定泡沫覆盖层，隔绝氧气，具有隔热、隔氧、阻止可燃气体向外逸出的作用，从而达到阻燃目的。如有机阻磷类阻燃剂受热时能产生结构更趋稳定的交联状固体物质或碳化层。碳化层的形成一方面能阻止聚合物进一步热解，另一方面能阻止其内部的热分解产生物进入气相参与燃烧过程。

3、 抑制链反应

根据燃烧的链反应理论，维持燃烧所需的是自由基。阻燃剂可作用于气相燃烧区，捕捉燃烧反应中的自由基，从而阻止火焰的传播，使燃烧区的火焰密度下降，最终使燃烧反应速度下降直至终止。如含卤阻燃剂，它的蒸发温度和聚合物分解温度相同或相近，当聚合物受热分解时，阻燃剂也同时挥发出来。此时含卤阻燃剂与热分解产物同时处于气相燃烧区，卤素便能够捕捉燃烧反应中的自由基，从而阻止火焰的传播，使燃烧区的火焰密度下降，最终使燃烧反应速度下降直至终止。

4、 不燃气体窒息作用

阻燃剂受热时分解出不燃气体，将可燃物分解出来的可燃气体的浓度冲淡到燃烧下限以下。同时也对燃烧区内的氧浓度具有稀释的作用，阻止燃烧的继续进行，达到阻燃的作用。

5 燃烧和阻燃的机理

在 3 节及表 3 和表 4 中，我们论述了决定纺织品纤维固有燃烧行为的基本热参量。为了了解现有纺织品阻燃剂如何起作用以及更重要的--如何研发未来的阻燃剂，关键是更为深入地探索成纤聚合物的燃烧机理。

5．1 阻燃策略

图 7 所示为纺织品燃烧机理(作为一种反馈机理)的过程，在这种燃烧中，燃料（来自热降解或热解纤维）、热（来自引燃和燃烧）和氧（来自空气）均作为主要成分发挥作用。为了中断这种机理，人们提出了 5 种方式（a）～（e）。阻燃剂可在其中的一种或多种方式下发挥作用。以下所列为各个阶段及相关的阻燃作用：

a）除热；b）提
高分解温度；
c）减少可燃挥发物的形成，增加炭量；d）减少与氧
的接触或稀释火焰；e）干扰火焰化学反应和/或提高
燃料点燃温度（Tc）；

熔解和/或降解和/或脱水需吸收大量的热（例如，在背涂层中含无机和有机磷的制剂、氢氧化铝或水化氧化铝）。通常不为阻燃剂所利用；而在固有耐火和耐热纤维（如芳族聚酰胺纤维）中较常见。纤维素和羊毛中多数含磷、含氮的阻燃剂；在羊毛中的重金属络合物。水合的及某些促炭阻燃剂可释放水；含卤素阻燃剂可释放卤化氢。含卤素阻燃剂，经常与氧化锑结合。从上述内容可以看出，某些类阻燃剂可以在多种方式下发挥作用，多数有效的例子都是如此。此外，某些阻燃制剂可产生液相中间物，该中间物可湿润纤维表面，从而成为隔热和隔氧的屏障--广为接受的硼酸盐-硼酸混合物即可在这种方式下发挥作用。此外，它还可促进成炭。

为了简化化学阻燃行为之不同方式的分类，可以使用术语'凝聚'相和'气或蒸汽'相活动来区分它们。二者都是复合项，前者包括上述的（a～c）方式，后者包括（d）和（e）方式。物理机理

通常同时起作用，这些机理包括通过形成涂层来排除氧气和/或热量（方式 d）、增加热容量（方式 a）以及利用非易燃气体稀释或覆盖火焰（方式 d）。

5．2 热塑性

纤维是否可以变软和/或熔化（由表 3 中的物理转化温度所界定）决定着它是否具有热

塑性。热塑性因其相关的物理变化，可严重影响阻燃剂的行为。传统的热塑性纤维（例如，聚酰胺、聚酯和聚丙烯）一收缩即可离开点燃火焰，从而避免被点燃：这使它们表面上显现出阻燃性。事实上，如果收缩受阻，它们便会猛烈燃烧。这种所谓的支架效应可在聚酯-棉以及类似的混纺织物上看到，即熔融聚合物熔化到非热塑性棉上并被点燃。类似的效应也可在由热塑性和非热塑性成分组成的复合纺织品上看到。

随着上述效应而来的是熔滴（通常是有焰熔滴）问题，这种滴淌虽可移除焰锋的热并促使火焰熄灭（因而可以'通过'垂直火焰试验），但却能使位于其下的表面（如地毯或皮肤）发生燃烧或二次点燃。

多数在批量生产期间或作为整理剂施用于传统合成纤维上的阻燃剂通常都是通过增强熔融滴淌和/或促助有焰熔滴熄灭两种方式发挥作用的。迄今为止，任何手段都不能降低热塑性并大量促进成炭，经阻燃处理的纤维素（包括粘胶纤维）的情况就是如此。

5．3 阻燃机理和成炭

按（d）和/或（e）方式在气相起作用的阻燃剂都具有下述优点，即它们会减小引燃倾向并有助于纺织品成纤聚合物的火焰熄灭。这是因为一旦热降解产生的挥发产物或燃料在火焰中与氧发生氧化反应，其化学性质就会变得非常类似。因此，像断绝氧气（（e）方式）或生成干扰自由基（（f）方式）这两种方式无疑都能保证阻燃剂的效果。

根据成本和效益，锑-卤素阻燃剂是本体聚合物和背涂层纺织品领域内最成功阻燃剂。与用于纤维素纤维的含磷和氮的纤维反应性耐久阻燃剂不同（见下文)，它们通常只能借助树脂粘合剂用作背涂层剂。就纺织品而言，多数锑-卤素体系都由三氧化二锑和含溴的有机分子（例如氧化十溴联苯（DBDPO）或六溴环十三烷（HBCD））组成。一经加热，这些物质就会释放出 HBr 基和 Br。基。这二者会根据下面的示意图干扰火焰的化学反应。在示意图中： R 、 CH2 、 H 和 OH 基是火焰氧化链反应的一部分，该反应消耗燃料（RCH3）和氧。

Detailed flame retardant flame retardant principle

Flame retardants exert their flame-retardant effects through several mechanisms, such as endothermic action, covering action, chain reaction inhibition, choking action of non-combustible gas, and the like. Most flame retardants work together through several mechanisms to achieve flame retardant purposes.

1, endothermic effect

Any amount of heat released during a short period of time is limited. If it absorbs a part of the heat released by the fire source in a relatively short period of time, the flame temperature will decrease, radiate to the combustion surface and act on the surface that will be vaporized. The amount of heat that cracks the flammable molecules into free radicals will decrease, and the combustion reaction will be suppressed to some extent. Under high temperature conditions, the flame retardant undergoes a strong endothermic reaction, absorbs part of the heat released by combustion, lowers the temperature of the combustible surface, effectively suppresses the formation of flammable gas, and prevents the spread of combustion. The flame retardant mechanism of $Al(OH)3$ flame retardant is to increase the heat capacity of the polymer, so that it absorbs more heat before reaching the thermal decomposition temperature, thereby improving its flame retardant performance. This type of flame retardant fully exerts the characteristics of large heat absorption when it combines water vapor, and improves its own flame retardant ability.

2, covering effect

After the flame retardant is added into the flammable material, the flame retardant can form a glassy or stable foam cover layer at high temperature, isolate the oxygen, have heat insulation, block oxygen, and prevent the combustible gas from escaping outwards, so as to achieve flame retardancy purpose. For example, when organic phosphorus-containing flame retardants are heated, they can produce more stable cross-linked solid materials or carbide layers. The formation of the carbonized layer on the one hand can prevent further pyrolysis of the polymer, and on the other hand can prevent the internal thermal decomposition products from entering the gas phase and participating in the combustion process.

3, inhibition of chain reaction

According to the combustion chain reaction theory, free radicals are needed to sustain combustion. The flame retardant can act on the gas-phase combustion zone, capture free radicals in the combustion reaction, thereby preventing the flame from propagating, reducing the flame density in the combustion zone, and ultimately slowing down the combustion reaction until termination. For example, halogen-containing flame retardants have the same or similar evaporation temperature and polymer decomposition temperature. When the polymer is decomposed by heat, the flame retardant also volatilizes at the same time. At this time, halogen-containing flame retardant and thermal decomposition products are in the gas-phase combustion zone at the same time. The halogen can capture free radicals in the combustion reaction, thus preventing the flame from propagating, reducing the flame density in the combustion zone, and eventually reducing the combustion reaction rate until termination. .

4, the role of non-gas smothering

When the flame retardant is heated, it decomposes the non-combustible gas and dilutes the concentration of the flammable gas that is decomposed by the combustibles to below the combustion lower limit. At the same time it also has a dilute effect on the oxygen concentration in the combustion zone, preventing the combustion from proceeding and achieving the flame retardant effect.

5 combustion and flame retardant mechanism

In Section 3 and Tables 3 and 4, we discuss the basic heat parameters that determine the inherent combustion behavior of textile fibers. In order to understand how the existing textile flame retardants work and, more importantly, how to develop future flame retardants, the key is to explore more deeply the combustion mechanism of fiber-forming polymers.

5.1 Flame Retardant Strategy

Figure 7 shows the process of a textile combustion mechanism (as a feedback mechanism) in which fuel (from thermal degradation or pyrolysis), heat (from ignition and combustion), and oxygen (from air) are Acts as a main ingredient. In order to break this mechanism, people have proposed five ways (a) to (e). Flame retardants can act in one or more of these ways. The following are listed for each stage and related flame retardant effects:

a) remove heat; b) increase decomposition temperature;

c) reduce the formation of combustible volatiles and increase the amount of carbon; d) reduce the contact with oxygen or dilute the flame; e) interfere with the flame chemical reaction and/or increase the fuel ignition temperature (Tc);

Melting and/or degradation and/or dehydration require the absorption of large amounts of heat (for example, formulations containing inorganic and organic phosphorus in the back coating, aluminum hydroxide or hydrated alumina). It is not normally used for flame retardants; it is more common in inherently flame resistant and heat resistant fibers such as aramid fibers. Most phosphorus and nitrogen-containing flame retardants in cellulose and wool; heavy metal complexes in wool. Hydrated and some charcoal-reducing agents release water; halogen-containing flame retardants release hydrogen halide. Halogen-containing flame retardants, often combined with lanthanum oxide. From the above, it can be seen that certain types of flame retardants can function in a variety of ways, as are most effective examples. In addition, certain flame-retardant formulations can produce liquid-phase intermediates that can wet the surface of the fiber, thereby acting as a barrier to thermal and oxygen barriers - the well-accepted borate-boric acid mixture can be used in this manner Play a role. In addition, it also promotes char formation. In order to simplify the classification of different ways of chemical flame-retarding behavior, the terms 'cohesion' phase and 'gas or steam' phase activity can be used to distinguish them. Both are composite terms. The former includes the above (a to c) modes, and the latter includes (d) and (e) modes. Physical mechanism

Often at the same time, these mechanisms include the exclusion of oxygen and/or heat (pattern d), the increase of heat capacity (pattern a), and the dilution or covering of the flame with a non-flammable gas (pattern d) by forming a coating.

5.2 Thermoplasticity

Whether the fiber can soften and/or melt (defined by the physical transition temperature in Table 3) determines whether it is hot

Plasticity. Thermoplastics can seriously affect the behavior of flame retardants due to their associated physical changes. Traditional thermoplastic fibers (eg, polyamides, polyesters, and polypropylenes) can leave the ignition flame as they shrink, preventing them from being ignited: this makes them appear flame-retardant on the surface. In fact, if the shrinkage is blocked, they will burn violently. This so-called stenting effect can be seen on polyester-cotton and similar blended fabrics, i.e. molten polymer melts onto non-thermoplastic cotton and is ignited. Similar effects can also be seen on composite textiles composed of thermoplastic and non-thermoplastic components.

With these effects comes the problem of droplets (usually flaming droplets) which remove the heat of the flame front and cause the flame to extinguish (thereby allowing 'vertical flame testing'), but Burn or re-ignite a surface (such as a carpet or skin) beneath it.

Most flame retardants that are applied to traditional synthetic fibers during batch production or as finishing agents are usually acted upon by enhancing the molten dripping and/or promoting flame extinguishing. To date, no means has been able to reduce thermoplastics and promote char formation in large quantities, as has been the case with flame-retarded cellulose (including viscose fibers).

5.3 Flame Retardant Mechanism and Charcoal Formation

Flame retardants that function in the gas phase in the manner of (d) and/or (e) have the advantage that they reduce the tendency to ignite and contribute to flame extinction of the textile fiber-forming polymer. This is because once the thermal degradation produces volatile products or fuels that undergo oxidation reaction with oxygen in the flame, their chemical properties will become very similar. Therefore, there are undoubtedly guarantees of flame retardant effects, such as the two methods of cutting off oxygen ((e) mode) or generating interference free radicals ((f) mode).

Based on cost and benefits, helium-halogen flame retardants are the most successful flame retardants in the field of bulk polymers and back coat textiles. Unlike the phosphorus- and nitrogen-containing fiber-reactive durable flame retardants used for cellulosic fibers (see below), they can usually only be used as backcoat agents with the aid of resin binders. In the case of textiles, most bismuth-halogen systems consist of antimony trioxide and bromine-containing organic molecules such as decabromobiphenyl (DBDPO) or hexabromocyclotridecane (HBCD). Upon heating, these materials release HBr groups and Br. base. Both of these will interfere with the chemical reaction of the flame according to the schematic below. In the diagram: R, CH2, H, and OH radicals are part of the flame oxidation chain reaction, which consumes fuel (RCH3) and oxygen.