Scented Polyolefins from Ziegler-Natta Catalysts

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Abstract

Each year, transition metal catalysts are used on six continents to manufacture millions of tons of polyolefins. Ziegler-Natta catalysts are, by far, the most important. Since the inception of the polyolefins industry based on Ziegler-Natta catalysts in the 1950s, aluminum alkyls have been indispensable. That remains so today. This paper describes aluminum alkyls that function as cocatalysts and leave residues in the polymer that are converted to compounds which impart a scent to the polymer. Suitable cocatalysts may be produced in-house from readily available precursors using well-established methods. Alternatively, such cocatalysts may be obtained from metal alkyl manufacturers.

Though scented polyolefins have been available for many years, techniques used to produce them have changed little. Typically, methods involve post-reactor blending of virgin resin with masterbatches containing aroma compounds [1]. This paper describes use of aluminum alkyls to produce scented polyolefins manufactured with Ziegler-Natta catalysts. A convenient way to illustrate the technology is to consider the case study of citronellol, also known as 3,7-dimethyl-6-octen-1-ol. Citronellol is a well-established scent compound with a floral, rose-like aroma and is used in perfumery and insect repellants. (Commercially available citronellol is a mixture of stereoisomers.) Cocatalyst may be produced by reaction of a terpene with triisobutylaluminum (TIBAL) using technology disclosed in expired patents by Karl Ziegler and discussed by Ziegler in an American Chemical Society review published in 1960 [2].

A crucial aspect of the method described here is as follows: After the raw polymer is exposed to ambient air, cocatalyst residues generate the scent agent in the usual course of the process. That is, after the polymer is produced, it is simply handled by standard procedures. Cocatalyst residues will oxidize and hydrolyze to produce scent compounds. Scent agents will be dispersed evenly throughout the polymer. Routine handling usually involves pneumatic conveyance and pelletization, during which the polymer is exposed to ambient air. Alternatively, simple steps (discussed below) may be taken to facilitate oxidation/hydrolysis of cocatalyst residues. In either case, post-reactor blending and masterbatches are obviated.

Scented polyolefins could add value to the millions of pounds of film used to produce trash bags, grocery bags and merchandise ("T-shirt") bags. Scents may also enhance marketability of disposable diapers and personal hygiene products.

Perhaps an even more important possible application is the life-saving potential of citronellol-scented polyolefin in insecticide-treated nets for prevention of diseases spread by mosquitoes. (Citronellol is a well-known mosquito repellant.)

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Background for This Paper

When I was just beginning my career as an industrial chemist in the 1970s, among my early assignments was to work with a company in the flavor and fragrance industry. The company wanted to explore whether an aluminum alkyl might afford advantages as a route to citronellol, a well-established F&F product. The project was a technical success and progressed to the plant trial stage, but economics did not warrant changing from their existing technology. The project was terminated.

The aluminum alkyl intermediate was assigned the moniker "tricitronellylaluminum" (TCAL, pronounced "tee cal," discussed below), but was never offered to the polyolefins industry for use as a cocatalyst. There were several reasons for this, including:

> ➢ TCAL was unproven as a cocatalyst for Ziegler-Natta catalysts,

> ➢ TCAL was costlier than conventional aluminum alkyl cocatalysts.

At the time, there was little incentive for polyolefin producers to evaluate TCAL as a cocatalyst for ZN polymerizations. We eventually tested TCAL using a supported ZN polyethylene catalyst. I recall that TCAL functioned reasonably well as a cocatalyst, though the activity was somewhat lower than results with triethylaluminum (TEAL). Polyethylene from the experiment was stored in a large evaporating dish in a vacuum desiccator jar. When the cover was removed, the polymer exuded the distinct scent of lemon. Since citronellol is reported to have a floral, rose-like aroma [3], the product may have been partially converted to citronellal, reported to have an intense lemon scent [4].

Though TCAL has received little attention for many years, the cursory experiment above demonstrated that TCAL and similar aluminum alkyls might be useful for introducing scents to polyolefins. The method constitutes a simple means of adding value to polyolefins for several niche applications, identified later in this paper. Technology used to produce TCAL and similar compounds is in the public domain, since relevant patents expired decades ago. The aluminum alkyls could be easily produced in-house or provided by existing industrial manufacturers of metal alkyls.

In recent years, I approached several companies that are either directly or indirectly involved in the polyolefins industry. None was interested in scented polyolefins, so I decided to appeal to a broader audience at the SPE conference on polyolefins.

What is the intent of this paper? My hope is to generate interest in a simple, convenient method to introduce scents to polyolefins for use in selected applications, for example, in LLDPE trash bags. Perhaps an even more important application is bed netting that may be produced with citronellol-scented polyolefin fibers which could potentially save lives in countries afflicted by mosquito-borne diseases, such as malaria, yellow fever and dengue fever. Such netting would be an environmentally friendly way of introducing mosquito repellant and obviate the soaking of nets in noxious insecticides. Other applications of scented polyolefins may occur to marketing experts in attendance at this conference. From a personal standpoint, it will be profoundly gratifying in my senectitude to play a role in bringing value-added products to market, particularly one that might save lives.

Introduction

The global plastics business is enormous. The demand in 2015 was estimated to have been about 240 million metric tons for the major plastics [5], or about 70 pounds for every man, woman and child in the world. Polyolefins accounted for nearly ⅔ of the total, or about 151 million metric tons. All industrial polyolefins require a catalyst or an initiator to effect the polymerization of ethylene and propylene. Transition metal catalysts are, by far, the most important, accounting for about 86% of the global output of polyolefins.

Polyethylene was first manufactured on a large scale in 1939 and the product was then known as "high pressure polyethylene" [6]. Now known as low density polyethylene (LDPE), it remains industrially important today, though it is largely peripheral to the motif of this paper. LDPE and closely related products, such as EVA (ethylene-vinyl acetate copolymer), are manufactured at high pressures and temperatures using free radical initiators, almost exclusively organic peroxides. All other versions of polyethylene (HDPE, MDPE, HMW-HDPE, LLDPE, etc.) and the various forms of polypropylene (HP, RCP and ICP) are produced with transition metal catalysts.

Dr. Clifford Lee, VP of Townsend Solutions, estimates that about 280 billion pounds of HDPE, LLDPE and PP were produced in 2015 [7]. HDPE, LLDPE and PP are fabricated into a diverse range of consumer goods using a variety of processing methods. For example, large amounts of (~80%) of LLDPE go into blown film applications. Significant amounts of HDPE (25-30%) and PP (15-20%) are also fabricated into film. Dr. Lee estimates that the global production of HDPE and LLDPE in 2015 was about 151 billion pounds and all forms of polypropylene totaled about 129 billion pounds [7].

Two types of transition metal catalysts account for the vast majority of polyolefins manufactured in the world today: Ziegler-Natta and chromium catalysts [8]. For HDPE, chromium supported on silica ("Phillips") catalysts are narrowly favored over Ziegler-Natta catalysts. In large measure, this is because chromium catalysts produce HDPE with broad molecular weight distribution which enhances processibility while retaining mechanical properties. It is estimated that slightly more than half of the global production of HDPE employs chromium catalysts. However, ZN catalysts are dominant in LLDPE, accounting for about 84% of the total. In polypropylene, ZN catalysts are even more dominant, accounting for more than 97% of total PP production. Collectively, for the manufacture of HDPE, LLDPE and PP, transition metal catalysts are used in the following approximate proportions:

Ziegler-Natta:	78%
Cr ("Phillips"):	17%
Single Site:	5%

Polyolefins incorporating fragrances have been described in the literature for many years. A case in point is a patent issued in 1971 disclosing post-reactor blending of polyethylene of small particle size with a scent agent [9]. Polyethylene particles were ground to a fine powder (200 mesh was preferred). A masterbatch was prepared by blending 30% of a fragrance compound with fine HDPE powder. The fragrance-containing masterbatch was then blended with virgin LDPE to achieve a polyethylene composition containing about 3000 ppm scent agent. Though the patent describes a process for production of scented polyolefins, there are significant differences relative to the process discussed in this paper:

➢ The method described in this paper does not require grinding or milling.

- ➢ Masterbatches containing 30-40% (300,000 to 400,000 ppm) of fragrance compounds are not required.

- ➢ Concentration of scent agent in the final polyolefin composition in the aluminum alkyl route is an order of magnitude lower.

Ziegler-Natta Catalysts

What are known today as "Ziegler-Natta catalysts" were discovered in 1953 by German chemist Karl Ziegler. Because a preliminary experiment with propylene was deemed to have been unsuccessful (a conclusion later realized to be in error), Ziegler decided to focus on ethylene polymerization and return to propylene later [10, 11]. Giulio Natta was then Director of the Institute of Industrial Chemistry at the Milan Polytechnic Institute and a consultant to Montecatini. In 1952, Natta attended a lecture delivered by Ziegler in Frankfurt during which he learned of Ziegler's success with the oligomerization of ethylene by the so-called growth ("aufbau") reaction [10]. (The "aufbau" reaction foreshadowed Ziegler's later discoveries on ethylene polymerization.) Natta influenced Montecatini to engage Ziegler as a consultant and to obtain commercial rights to Ziegler's technology in Italy. The consulting agreement allowed Natta access to Ziegler's discoveries on what was termed "transformation of olefins." Using catalysts described by Ziegler for ethylene polymerization, Natta polymerized propylene and determined the crystal structure of stereoregular polypropylene. This work was done before Ziegler had returned to study the applicability of his catalysts to propylene polymerization. This sequence of events ended the previously close personal relationship between Ziegler and Natta [10]. Nonetheless, Ziegler and Natta were jointly awarded the 1963 Nobel Prize in chemistry. Today, ZN catalysts are used globally for production of millions of tons of polyethylene and polypropylene.

Ziegler-Natta catalysts may be broadly defined as binary combinations of a transition metal compound from Groups 3-12 of the Periodic Table with an organometallic compound from Groups 1, 2 or 13 [12]. Substantial reactions take place between the transition metal and organometallic components resulting in predominantly inorganic compositions that function as polymerization catalysts. Many modern ZN catalysts are produced using titanium tetrachloride ($TiCl_4$, or "tickle 4") and TEAL, both clear, colorless liquids. Though $TiCl_4$ is sometimes (erroneously) called the "catalyst," it is more accurate to call $TiCl_4$ a "pre-catalyst," since it must be transformed through reactions with TEAL. Independently, neither $TiCl_4$ nor TEAL is capable of producing high polymers in practical amounts. Moisture and air must be rigorously excluded during handling of ZN catalysts, because even small (ppm) amounts of water and oxygen may result in deactivation ("poisoning") of the catalyst. Industrial ZN catalysts are often supported on silica or magnesium chloride.

Early industrial Ziegler-Natta catalysts were obtained principally by reduction of $TiCl_4$ using aluminum metal. They were unsupported and contained occluded $AlCl_3$. These archaic catalysts were powdery, purple solids containing about 24%Ti, and exhibited low activity (usually < 2 kg polymer/g catalyst). Because of low activity, polymer produced with these primitive catalysts required post-reactor treatment to remove catalyst residues and other undesirable components.

Modern ZN catalysts are typically powdery or granular solids with a grayish or brownish tint, depending on the transition metal, the support employed and activation procedure used. Many involve titanium and are produced by techniques that enable control of

morphology and particle size. Most contain only 1-4% titanium, but provide high activities. For example, activities as high as 100 kg of PP/g of catalyst [13] have been reported (corresponding to *millions* of pounds of PP per pound of titanium). The polymers require no post-reactor treatment to remove catalyst and cocatalyst residues.

Aluminum Alkyls

Aluminum alkyls have contributed mightily to the astonishing commercial success of Ziegler-Natta catalysts, harking back to the very beginning of the polyolefins industry based on transition metal catalysts. The most important aluminum alkyl in the polyolefins industry today is TEAL, sold globally in multi-million pound/year quantities. However, TEAL and most of the industrially important aluminum alkyls are very hazardous chemicals. TEAL is both pyrophoric (ignites on exposure to air) and explosively reactive with water, as are many of the commercially significant aluminum alkyls.

Aluminum alkyl cocatalysts for ZN polymerizations are typically used in large excess relative to the transition metal. Al/transition metal ratios of 30-40 are not uncommon in industrial polyethylene processes. An excess is used to insure that sufficient aluminum alkyl is present to accomplish the three key roles that cocatalysts must fulfill [14]:

➢ Reduction of the transition metal compound to a lower oxidation state;

➢ Alkylation of the transition metal to produce active centers for polymerization;

➢ Scavenging of catalyst poisons, particularly water and oxygen.

Aluminum alkyls envisioned for introducing scents into polyolefins are significantly less hazardous than TEAL. They contain lower Al content and will be much less reactive with air and water. The aluminum alkyl selected for the case study is tris(3,7-dimethyl-6-octenyl)aluminum, known more simply as "tricitronellylaluminum" (TCAL). TCAL may be produced using the so-called exchange (or displacement) reaction of TIBAL with the terpene 3,7-dimethyl-1,6-octadiene ("citronellene"), chemistry developed by Ziegler in the 1950s [2, 15]. The internal double bond is virtually unreactive under conditions commonly used for exchange reactions.

"citronellene"
(3,7-dimethyl-1,6-octadiene)

TCAL

citronellol
(3,7-dimethyl-6-octen-1-ol)

chiral carbon atom

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TCAL is a non-viscous liquid with formula weight of 444.8 and a theoretical aluminum content of 6.07%. Handling characteristics are similar to that of a Grignard reagent. Though TCAL is air- and water-reactive, it is substantially less hazardous than TEAL. For example, the non-pyrophoric limit (NPL) of TCAL in heptane is 91%, while the NPL of TEAL in heptane is 12% (higher NPLs indicate lower reactivity [16]). The NPL of TCAL is comparable to that of the mildly air-reactive tri-*n*-decylaluminum.

The approximate concentration of citronellol within a polyolefin may be calculated using a hypothetical ethylene polymerization with a Ziegler-Natta catalyst, TCAL cocatalyst and the following assumptions:

➢ the catalyst contains 1.5% titanium

➢ the cocatalyst (TCAL) contains 6.0% Al

➢ the Al/Ti ratio used in the polymerization is 40, and

➢ the activity of the catalyst is 20,000 lb polymer/lb of catalyst.

In this illustration, the final concentration of TCAL in the polymer will be about 280 ppm. In theory, one mole of TCAL will generate 3 molar equivalents of citronellol. However, yields of alcohols *via* oxidation-hydrolysis of R_3Al compounds are known to be lowered because of free radical side reactions [17], one of which produces an aldehyde (perhaps explaining the intense lemon scent characteristic of citronellal mentioned earlier). Free radical side reactions can be minimized by introduction of catalytic amounts of titanium compounds, such as tetraisopropyl titanate (TIPT), enabling yields of >90% to be obtained [17]. Allowing for yield losses from side reactions, it is estimated that the concentration of citronellol dispersed within the polyethylene of this illustration will be about 260 ppm. The "aroma threshold limit value" for detection of citronellol is reported to range from 11 ppb to 2.2 ppm [18].

If the scent is too pronounced, the cocatalyst may be diluted with a less expensive cocatalyst such as TEAL. If concentration of scent agent needs to be increased, higher Al/transition metal ratios may be used. Ratios of 100-200 will lower polymer molecular weight marginally owing to chain transfer reactions, but should have little impact on other polymer properties. Another way to maximize scent agent would be to carry out simple post-reactor steps (though masterbatches would still not be required). For example, addition of a catalytic amount of TIPT, subsequently sparging the raw polymer with dry air, and then with water mist, should increase the concentration of scent agent.

Using selected aluminum alkyls to impart scent to polyolefins may be demonstrated in small-scale polymerization tests with standard Ziegler-Natta catalysts from a range of polyolefin technologies, including Unipol®, Spheripol®, Borstar® and Hypol®. Initial demonstration of the method could be done in laboratory or pilot plant polymerization reactors [19].

Scope

Citronellol is but one of several agents that may be used to impart a pleasant scent to polyolefins by way of aluminum alkyl cocatalysts. For example, suitable cocatalysts may be prepared by reaction of TIBAL with other terpenes or different organic compounds containing a terminal double bond. As in the TCAL case study, internal double bonds will

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be essentially unreactive. In many respects, aluminum alkyls derived from terpenes will be similar to conventional R_3Al compounds. Since TCAL and the aluminum alkyls obtained from terpenes illustrated below contain no functional groups that might interfere with their performance as ZN cocatalysts, they should perform reasonably well in olefin polymerization. For interested parties, samples of scented aluminum alkyl cocatalysts can be arranged for testing.

Limonene is a cyclic terpene with the scent of oranges. It is obtained from the rinds of citrus fruits. Like citronellene, it is commercially available and can be easily converted into an aluminum alkyl that will be effective as a cocatalyst for ZN catalysts. After aging in air (and undergoing oxidation and hydrolysis), the scent compound in the polymer will be 2-(4-methylcyclohex-3-en-1-yl)propan-1-ol, also known as "p-menth-1-en-9-ol", which has a distinctive fruity, herbal note.

limonene
(scent of oranges)

p-menth-1-en-9-ol
(fruity, herbal note)
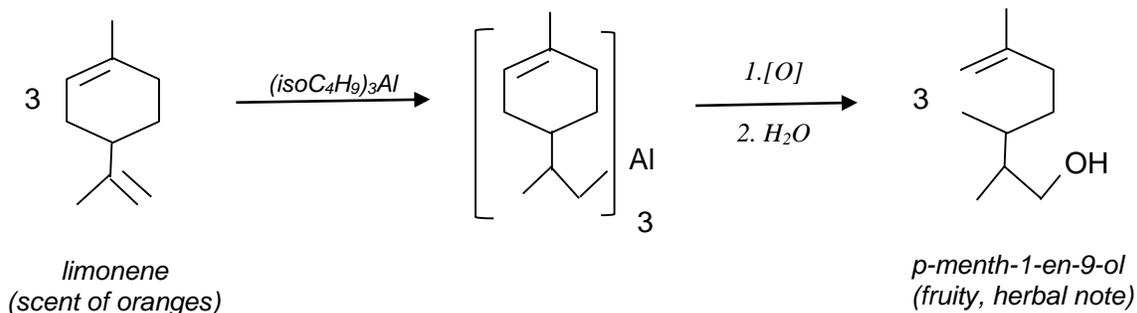
β-Pinene is another commercially available cyclic terpene that may be readily converted into an aluminum alkyl cocatalyst. β-Pinene is obtained from pine resin and possesses a "woody, green pine-like smell" [20]. After polymerization, the aluminum alkyl will produce myrtanol which is used in perfumery and as a flavorant:

β-pinene
(woody, green scent)

myrtanol
(used in perfumery and as flavorant)
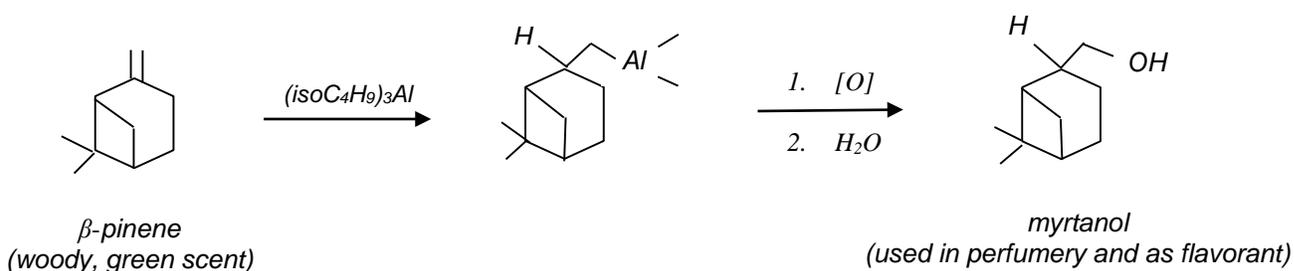
An unknown in the method disclosed here is the extent to which the scent compound may decompose during high temperature processes typically used for extrusion of polyolefins. Temperatures in excess of 200° C are routine. Like citronellol, 1-decanol (*n*-decyl alcohol) is a primary C_{10} alcohol with comparable formula weight (158.2), and is reported to decompose between 299 and 393 °C [21]. Furthermore, the atmospheric boiling point of citronellol is reported to be 225° C [22]. These data suggest that thermal stability of citronellol may not be a significant issue.

Applications

Scented polyolefins will be suitable primarily for niche markets. Key targets are polyolefin films that are fabricated into bags, personal hygiene products and other consumer goods to which a pleasant scent may add value. However, for most large-volume markets for HDPE, LLDPE and PP, scents will be superfluous. If applications are successfully developed, scented polyolefins will likely be manufactured in campaigns using standard ZN catalysts and polymerization reactors. Manufacturing facilities may be converted back to unscented products simply by dropping in a conventional cocatalyst, such as TEAL, into the process.

Polyolefin Film

Polyolefin film has been fabricated into trash bags with pleasant scents for many years. Fragrances mask malodorous refuse in trash bags. Heretofore, scents have typically been introduced by way of masterbatches in post-reactor treatments [1, 9]. Polyolefin film is also used to fabricate grocery and merchandise bags, both of which are eminently recyclable. Scents should not adversely affect recyclability of polyolefin films. (However, today only small quantities of plastic bags are recycled. Reasons for low recycle rates are varied, but include inadequate infrastructure, marginal economics and limited markets for recycled products.)

Personal Hygiene Products

Polyolefins are used to produce personal hygiene products, such as incontinence pads and sanitary napkins. They are also used in disposable diapers. Polyolefins with a scent should mitigate offensive odors from such products.

Artificial Flowers

Though a relatively small-volume application, polyolefins are used in production of artificial flowers. A pleasant scent should enhance marketability of decorative flowers.

Mosquito Bed Netting

Mosquito-borne diseases have tormented humankind for thousands of years [23]. Ancient Chinese writings described symptoms of the illness that would later become known as malaria. Malaria is spread by *Anopheles* mosquitoes infected with protozoan parasites, most notably *Plasmodium falciparum*. According to the World Health Organization (WHO, the global health organization of the United Nations), deaths from malaria in 2015 were about 438,000 [24]. However, annual worldwide deaths from malaria in the millions were not uncommon as recently as the 1930s.

Moreover, mosquitoes spread other deadly diseases such as yellow fever. An article in a chemical industry trade magazine reported in early 2016 that more than "1 million people die [annually] from mosquito-borne illnesses" [25]. Prevention of mosquito bites may save millions of lives. Mosquitoes (*Aedes aegypti*) are also responsible for spreading the Zika virus. (Though Zika causes the heartrending birth defect called microcephaly, it is rarely fatal.)

In the latter part of World War II, "dichlorodiphenyltrichloroethane" (DDT) saved the lives of innumerable servicemen in areas afflicted by malaria [26]. After the war, DDT virtually eliminated malaria in some Third World countries. Illustrative is the case history of Sri

Lanka (formerly Ceylon), a small island country about the size of West Virginia located off the southeast coast of India. Sri Lanka's history shows the ebb and flow of the dread disease over the past century. In Ceylon/Sri Lanka, DDT use began in 1946 and had nearly eliminated malaria by 1963 [27]. Resurgence of the disease occurred in the late 1960s owing to a variety of factors, including scaling back of indoor residual spraying (IRS) with DDT.

In the USA, a cooperative program involving the Center for Disease Control (CDC) and other public health agencies eliminated malaria by the late 1940s, primarily using DDT and IRS [28]. However, DDT was banned in the USA in 1972 by the first director of the EPA, William Ruckelshaus. Following the lead of the USA, other countries also banned DDT. Some Third World countries came under pressure from the USA and other major donors, who threatened to withhold food aid unless the country stopped using DDT [29]. In 2009, the United Nations stated its intent to phase-out DDT globally "by the early 2020s" [30]. Nonetheless, DDT is still being used for IRS in developing countries under exemptions from the Stockholm Convention on Persistent Organic Pollutants [31].

In the late 1950s, mosquitoes began to develop resistance to DDT [32], mostly a consequence of indiscriminate, large-scale misuse in agriculture. Because of incipient mosquito resistance and DDT bans, it has become imperative to develop alternative methods to combat malaria and other mosquito-borne illnesses.

A key alternative method involves use of nets that serve as a physical barrier to mosquitoes. Nets are intended for use over beds at night when female *Anopheles* mosquitoes seek blood meals for egg production. Insecticide-treated nets (ITN) are far more effective than untreated nets because, in addition to serving as a barrier, ITN repel and kill mosquitoes. Most bed nets are produced from polyethylene, polypropylene or polyester fibers [33]. To prepare ITN, nets are simply immersed in a water-insecticide bath and allowed to dry in air. Consequently, insecticide is merely deposited on the surface of the polymer. According to the CDC and WHO, only pyrethroids are approved for ITN at this point [33, 34].

"Mosquito nets are now a billion-dollar industry, with hundreds of millions of insecticide-treated nets passed out in recent years…" [35]. Though the latter statement may be hyperbole, it is clear that mosquito nets are vital in today's fight against malaria. Unfortunately, ITN meant to prevent nocturnal mosquito bites are being misused as fishing nets in Madagascar and other Third World countries [35].

Despite the fact that citronellol repels mosquitoes [22], it is not presently used in ITN. The principal reason is probably that citronellol is simply too volatile to exhibit longevity in ITN prepared by the immersion method. However, citronellol generated by the aluminum alkyl cocatalyst method will be uniformly distributed throughout the polymer (rather than merely deposited onto the surface, as in the immersion process). Scent agent will migrate to the surface by a process called "blooming." Instead of evaporating from the surface, it is believed that the scent agent will be slowly exuded from the polymer. Such ITN will release citronellol continually over an extended period, though long-term efficacy will have to be determined by further research. An additional advantage of ITN made from citronellol-impregnated fibers is that misuse as fishing nets would be less damaging environmentally compared to ITN produced using deleterious insecticides.

As a means of overcoming mosquito-resistance, WHO recently recommended that *two* insecticides be used in mosquito nets "to mitigate the risk of the development and

spread of insecticide resistance..." [34]. One of the insecticides in two-component ITN should be a citronellol-impregnated polyolefin fiber described here.

Regulatory

Judicious choice of scent agent may render regulatory barriers irrelevant. In the case study discussed above, for example, citronellol is the scent agent. Since citronellol is on the Federal Drug Administration's "generally regarded as safe" (GRAS) list, citronellol-scented polyolefins should pose few regulatory problems.

In the section on scope above, raw materials limonene and β-pinene are also on the GRAS list and are obtained from natural sources (citrus rinds and pine oil, respectively). Furthermore, the derivatives themselves (*p*-menth-1-en-9-ol and myrtanol) are used in perfumery and food additives, implying that regulatory obstacles should be minimal.

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