A CHINACOAT® CONFERENCE
中国国际涂料展指定学术会议

14-15.11.2017 ● 上海新国际博览中心
Shanghai New Int'l Expo Centre (SNIEC), China

应用于新型涂料的配方和新技术

Emerging Technologies & Formulations for Innovative Coatings

会议主题 Papers included:

- 抗菌涂料 Antimicrobial
- 腐蚀感应涂料 Corrosion Sensing
- 抗藻和耐沾污涂料 Dirt & Algae Resistant
- 易清洗 / 自清洁涂料 Easy / Self-cleaning
- 有机 / 无机杂合技术 Hybrid Organic/ Inorganic
- 创新涂料与技术 Innovative Coatings
- 多功能涂料 Multi-functional Coatings
- 超疏水涂料 Superhydrophoblic
- 可持续的环保涂料 Sustainable Coatings

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Prof. Jamil Baghdachi 教授
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Expo 新展星展览(深圳)有限公司 NEW EXPOSTAR (SZ) CO., LTD.

CHINACOAT EXHIBITION LTD. 中国国际涂料展有限公司

大会指定会刊 Official Publication

ITE SINOSTAR-ITE INT'L LTD. 中贸推广-艾特怡国际有限公司

PCI 中文版 Paint & Coatings Industry

香 港 HONG KONG (852) 2865 0062 • 上 海 SHANGHAI (86 21) 6150 4989 / 5877 7680 • info@sinostar-intl.com.hk

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应用于新型涂料的配方和新技术
Emerging Technologies & Formulations for Innovative Coatings

14. 11. 2017 (星期二 Tuesday)

09:00 - 09:30 与会者登记 Registration

09:30 - 10:00 **开幕演讲 OPENING SPEECH**
新型涂料的技术 Emerging Technologies in Coatings

第一节 Session I 多功能和可持续的环保涂料及助剂 Multi-functional, Sustainable Coatings & Additives

10:00 - 10:45 **主题论文 KEYNOTE PAPER 1**
有机—无机杂化功能聚合物涂料
Organic / Inorganic Hybrid Functional Polymer Coatings

10:45 - 11:00 茶歇 Coffee Break

11:00 - 11:35 **论文 PAPER 2**
水性有机 / 无机杂化体系—用于水性双组分锌粉涂料的创新型环保型树脂
Water-borne Organic / Inorganic Hybrid Systems – Innovative Binders for Environmentally Friendly Two Pack Zinc Dust Paints

11:35 - 12:10 **论文 PAPER 3**
一种新型环境友好型水性阳离子抗菌底漆
Waterborne Cationic Polymers – an Innovative, Eco-friendly Binder Technology for Primers & Antimicrobial Coating Applications

12:10 - 12:45 **论文 PAPER 4**
可提高多层涂装体系重涂性的一种独特新方法
A New & Unique Opportunity to Favor Overcoatability in Multi-Layer Systems

12:45 - 14:00 午餐 Lunch

第二节 Session II 耐候、抗藻和耐沾污涂料、抗菌、腐蚀感应涂料 Weather, Dirt & Algae Resistant, Anti-bacterial & Corrosion Sensing

14:00 - 14:35 **论文 PAPER 5**
超级耐沾污涂料的发展
Developments in Super Dirt Pickup Resistant Coatings

14:35 - 15:10 **论文 PAPER 6**
水性 PVDF 涂料技术：中国最新环境法规的解决方案
Waterborne PVDF Coatings Technology to Address the New Environmental Regulation in China

15:10 - 15:25 茶歇 Coffee Break

15:25 - 16:00 **论文 PAPER 7**
磺化石墨烯 / 水性聚氨酯涂料的耐腐蚀性能研究
Improved Corrosion Resistance Based on Sulfonated Graphene / Waterborne Polyurethane Coatings

16:00 - 16:15 公开论坛 Discussion Session

16:15 第一天完 End of Day 1

第一节 SESSION I 多功能和可持续的环保涂料及助剂 Multi-functional, Sustainable Coatings & Additives

14.11.2017 (星期二 Tuesday) • 09:30 – 12:45

武利民教授 Prof. Limin Wu
中国复旦大学
Fudan University, China

有机—无机杂化功能聚合物涂料
Organic / Inorganic Hybrid Functional Polymer Coatings

主题论文 KEY NOTE 1

近年来，我们发展出一系列新的方法来构筑功能胶体微球，并将这些纳米胶体微球用于制备功能涂料。例如，以曲拉通 X-100 改性的纳米 SiO_2 和 TiO_2 颗粒为 Pickering 乳化剂，苯乙烯、二甲基丙烯酸乙二醇酯、氟硅烷 (FAS) 以及引发剂等为油相，通过 Pickering 乳液聚合制备了包覆 FAS 的 UV 刺激响应性微胶囊。在 UV 光照下，微胶囊的聚合物壳层由于 TiO_2 的光催化降解作用而破裂，从而释放出 FAS 疏水物质，调节微胶囊中 TiO_2 的量可控制 FAS 的释放速度。该微胶囊可直接用于水性涂料，能够使涂层保持长时间的疏水性，具有自修复功能。将聚合物乳胶粒子与纳米二化硅共混成膜，通过改变聚合物胶体微球的尺寸大小，可制备出一系列结构色涂层。将列举例子来展示我们近几年在这方面的工作进展。

In recent years, we have developed several approaches to overcome these application drawbacks of nanoparticles. For example, Fluoroalkyl silane (FAS)-loaded polystyrene microcapsules were prepared via Pickering emulsion polymerization using silica/titania nanoparticles as Pickering agents, wherein the nanoparticles were first modified with a Trixton X-100-tethered silane coupling agent. Under UV exposure, the microcapsules break up and release the encapsulated FAS, demonstrating its UV-responsive ability. The releasing rate of FAS could be tuned by the content of TiO2 nanoparticles in the microcapsules. Moreover, these microcapsules can be embedded into waterborne coatings and prolong the hydrophobic performance of the coatings especially those used outdoors, such as waterproof, anti-icing and anti-flashing coatings; We also used polymer latex and silica nanoparticles to fabricate structural color coatings. Through adjusting the diameters of polymer colloids, coatings or films with various colors can be fabricated. Some examples will be given to demonstrate the recent works in my group.

15. 11. 2017 (星期三 Wednesday)

13:30 - 13:50 与会者登记 Registration

第三节 Session III 创新涂料与技术趋势 Innovative Coatings & Technology Trends

13:50 - 14:50 **主题论文 KEYNOTE PAPER 8**
涂料的化学与工艺的未来：需求与解答 / 新性能
The Future of Coatings Chemistry & Processes: Needs & Answers / New Performances

14:50 - 15:05 茶歇 Coffee Break

15:05 - 15:40 **论文 PAPER 9**
一种新型自修复涂料制备及其修复行为研究
Preparation & Self-healing Behaviors of a New Self-healable Coating

15:40 - 16:15 **论文 PAPER 10**
基于点击化学的结构型抗菌水性聚氨酯合成与表征
Synthesis & Characterization of Structural Anti-bacterial Waterborne Polyurethane via Click Chemistry

16:15 - 16:30 公开论坛 Discussion Session

16:30 - 16:50 闭幕辞 Closing Remarks

16:50 会议结束 End of Conference

* 论文的演讲和讨论将以英语和普通话进行。All presentation of papers & post presentation discussion will be conducted in both English & Chinese (Putonghua).
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高志晓 Frank Gao
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论文 PAPER 2

水性有机 / 无机杂化体系 — 用于水性双组分锌粉涂料的创新型环保型树脂

Water-borne Organic / Inorganic Hybrid Systems – Innovative Binders for Environmentally Friendly Two Pack Zinc Dust Paints

创新通常由市场需求来驱动，其中有些市场需求是因为环境问题引发的结果。新型水性有机 / 无机杂化体系的开发正是为了满足市场对零 VOC 涂料体系的需求。现实中水性涂料已经在市场上使用了相当长的时间，但是水性有机 / 无机杂化体系作为水性锌粉涂料的树脂的应用却是新的技术。该技术结合了有机和无机体系的优点，为重防腐应用提供优异的腐蚀防护性能，同时涂料配方可以满足最新的环保要求。这类型的水性锌粉涂料与面漆有优异的层间结合力，典型的面漆体系如：溶剂型环氧或水性环氧涂料。

水性有机 / 无机杂化体系的涂料配方具有以下优点：几乎零 VOC；低温固化；可同时满足低膜厚或高膜厚的应用需求；比单纯的有机涂层具有更好的耐热性；与面涂层间有良好的附著力；优异的腐蚀防护性能；

Innovations are often driven by market needs and some of the market needs are a result of environmental problems. New water-borne organic/inorganic hybrid systems were developed because of a market demand for VOC free coating systems. Water-borne coatings have been available for a long time but water-borne organic/inorganic hybrid systems as binders for zinc dust paints are new. They combine the advantages of the organic and inorganic world and formulations offer new environmentally friendly possibilities for heavy corrosion protection formulations with excellent performance. Water-borne zinc dust paints based on these organic/inorganic hybrid systems can be over coated e.g. with solvent and water-borne epoxy coatings.

The advantages of formulations based on such an organic/inorganic hybrid system like can be summarized as: almost VOC free, low temperature curing, low or high film thicknesses are possible, improved heat resistance compared to organic coatings, good adhesion to top coat and excellent corrosion protection performance

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DSM Coating Resins, The Netherlands

论文 PAPER 3

一种新型环境友好型水性阳离子抗菌底漆

Waterborne Cationic Polymers – an Innovative, Eco-friendly Binder Technology for Primers & Antimicrobial Coating Applications

阴离子型水性树脂中得到广泛的应用。然而，大部分应用于水性涂料的基材和颜料都带负电荷，因此涂覆在这样的基材或使用这样的颜料时，阳离子型树脂会是一个较好的选择。本文将阐述一种新型阳离子水性树脂技术会并展示其独特的性能。

该技术的独特性在于其非持久性作用的阳离子特性。阳离子电荷可提供普适性的附着力。在涂料干燥过程中，阳离子电荷的损失会释放一部分碱性基团与木材中渗出的单宁酸反应，从而提供两者之间优异的结合性能。这种非持久性阳离子树脂技术使水性单组分树脂代替油性双组分树脂用作封闭涂料成为可能。

已研究出一种持久性阳离子树脂技术。季铵盐基团的存在提高了对革兰氏阴性菌和革兰氏阳性菌的抗菌性。这种概念的独特性在于引入了具有共价键结构的季铵盐组分，获得一种不会被淋洗出的涂料，在反复清洁后依然可显示出持久的抗菌性。

Anionically stabilised waterborne binders are widely used. However, most of the substrates and most of the pigments used in waterborne paints carry a net negative charge. To adhere to such substrates or interact with such pigments, cationically stabilized binders rather than anionically stabilized ones would be a better choice. In this paper, we present an innovative waterborne cationic binder technology that offers unique advantages.

The uniqueness of this binder technology lies in its non-permanent cationic character. The cationic charge provides universal adhesion properties. Upon drying of the coating the loss of the cationic charge release a basic moiety that locks acidic tannins that exude from wood proving excellent knot bleeding. This non-permanent cationic binder technology makes it possible to replace solventborne two-component binders with waterborne one-component binders.

A permanent cationic binder technology has been developed. The presence of quaternary ammonium groups results in antimicrobial activity against gram+ and gram- bacteria. The uniqueness of this concept is the covalent incorporation of the quaternary ammonium groups. As result a non-leaching coating is obtained that exhibits a lasting antimicrobial effect that is maintained after repeated cleaning actions.

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论文 PAPER 4

可提高多层涂装体系重涂性的一种独特新方法

A New & Unique Opportunity to Favor Overcoatability in Multi-Layer Systems

当今的涂料技术由许多技术及商业挑战所带动。助剂作为涂料配方中重要成分可以使相关材料增值并推动技术进步。表面性能—如流平、滑爽、易清洁、可再涂性、疏水性或亲水性—受表面助剂的强烈影响。这些助剂通过向涂层—空气或涂层—基材介面迁移，从而改变表面或界面性能。这些助剂对涂层性能的影响取决于它们的化学成分及其结构。本次讲座将展示复杂的助剂技术，其高度结构化的聚合物结构来源于大分子单体技术。它将呈现通过使用亲水性助剂来提高多层涂装系统中后续涂层的润湿和流平的独特概念。我们将阐述三代助剂的演变过程和相关的工业应用的案例。第一种是常规的表面助剂，如标准聚丙烯酸酯，简单地改善流平性，最后是复杂结构的助剂（如接枝和高度支化的聚丙烯酸酯），与其它表面助剂不同，它不仅可以增加涂层的表面能，同时还可提供抗锁孔性能。

Today's coatings technology is driven by a number of technical and commercial challenges. Additives being important ingredients in the formulation of coatings are used to valorize the related materials and advance the technology. Surface properties – such as leveling, slip, ease of cleaning, recoatability, hydrophobic or hydrophilic properties – are strongly influenced by the surface-active additives. These additives migrate toward the coating-air or coating-substrate interface and tailor the surface or interface properties. The performance and properties that these additives attribute to the coating depend on their chemical compositions and their structures. This presentation will show sophisticated additive technologies, with their highly structured polymer architectures derived from the macromonomer technology. It will present a unique concept of using hydrophilic additives to favor the wetting and leveling of the subsequent coating layer in multilayer coatings. We will illustrate the evolution of the current technology over the course of three generations of additives with examples of industrial applications. The first are surface additives such as standard polyacrylate that simply ameliorate the leveling and the last are sophisticated architectures (such as graft and highly branched polyacrylates) which – unlike other surface additives – can, not only increase the surface energy, but also additionally provide anti-crater properties to coatings.

第二节 SESSION II 耐候、抗藻和耐沾污涂料、抗菌、腐蚀感应涂料

Weather, Dirt & Algae Resistant, Anti-bacterial & Corrosion Sensing

14.11.2017 (星期二 Tuesday)
14:00 – 16:15

寿晓海 Roger Shou*
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Larry Schnieders
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论文 PAPER 5

超级耐沾污涂料发展

Developments in Super Dirt Pickup Resistant Coatings

砖石涂料的耐沾污性能非常重要，这是由于其对建筑物结构美学的影响。能较长时间耐沾污的建筑物可以维持其美学吸引力且无需频繁地重新涂装。减少重新涂装的频率可以极大地降低建筑物维修保养的成本。

随着城市和城镇地区的扩大，空气中的灰层和颗粒物质的含量也有所增加。这些更具挑战性的环境条件迫使开发的聚合物需要具有更强的耐沾污性能。如预期一样，耐沾污性能的提高必须在不牺牲其它性能，如低温柔韧性和伸长率的情况下实现。

本文将介绍在最小化影响涂层其它性能的情况下，提高垂直弹性涂层耐沾污性能方面取得的进展。

Dirt pickup resistance of masonry coatings is important due the impact it has on the aesthetics of the structure. Structures that resist dirt pickup longer periods of time retain their aesthetic appeal and require less-frequent repainting. Reducing the frequency of repainting can significantly lower the maintenance cost of the structure.

As cities and urban areas have expanded, there has also been an increase in the amount of airborne dirt and particulate material1. These more challenging environmental conditions have forced the development of polymers with increased levels of dirt pickup resistance. As expected the increased din pickup resistance must be achieved without sacrificing other properties, such as low temperature flexibility and elongation.

This paper will present the progress made to increase dirt pickup resistance of vertical elastomeric coatings while minimizing the impact on other properties of the coating.

余鸿恩博士 Dr. An Du
美国阿科玛 Arkema Inc., USA

论文 PAPER 6

水性 PVDF 涂料技术：中国最新环境法规的解决方案

Waterborne PVDF Coatings Technology to Address the New Environmental Regulation in China

众所周知，PVDF (Polyvinylidene fluoride) 由于其优异的抗老化耐久性和耐化学性而被广泛应用于涂料市场。本文主要关注研发的水性 PVDF 树脂。该水性技术涂料被证明同传统的溶剂型涂料拥有相似的抗老化性能，不含有氟表面活性剂，可以应用于金属基材。水性 PVDF 树脂也符合诸如 AAMA 2605 等标准的严苛测试。该水性技术的生态友好性将很好的应对溶剂型树脂涂料配方中的 VOC 含量问题，在不牺牲涂料性能的同时，满足目前中国越来越严苛的环保法规。

Polyvinylidene fluoride (PVDF) is well-known in coatings applications for its excellent weatherability, durability and chemical resistance. This paper focuses on the innovation of waterborne PVDF resins. The waterborne technology is proven to have similar weatherability and durability performance to the traditional solvent-based technology. It is produced by a fluorosurfactant-free process and can be used on metal substrates with a similar application condition as solvent-based coatings. Formulations with the waterborne PVDF resins can pass various standards, such as AAMA 2605. The waterborne technology is an eco-friendly solution to address the VOC content in coatings and to meet the current environmental regulation in China without sacrificing coating performance.

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磺化石墨烯 / 水性聚氨酯涂料的耐腐蚀性能研究

论文 PAPER 7

Improved Corrosion Resistance Based on Sulfonated Graphene / Waterborne Polyurethane Coatings

本论文采用偶联剂对磺化石墨烯 (SG) 进行了改性，制备水性聚氨酯 (WPU) 涂料。利用傅立叶转换红外光谱、x 射线衍射和扫描电镜对磺化石墨烯的化学结构进行了表征。研究聚氨酯涂料的耐水和有机溶剂性、热稳定性、机械性能以及石墨烯在聚氨酯中的分散性能。最后，通过极化曲线和盐雾试验，对涂层的耐蚀性进行了表征。

In this paper, sulfonated graphene(SG) was modified by coupling agent, a series of waterborne polyurethane(WPU) coatings were prepared. The chemical structure of SG was characterized via Fourier-transform infrared (FT-IR) spectroscopy, X-Ray Diffraction (XRD) and scanning electron microscope (SEM). The performance of WPU film included water and organic solvent resistance, thermal stability, and mechanical properties as well as SEM imaging of the film surface were characterized in order to get the dispersion of SG. At last, the corrosion resistance of the coating was characterized by polarization curve and salt spray test.

第三节 SESSION III 创新涂料与技术趋势
Innovative Coatings & Technology Trends

15.11.2017（星期三 Wednesday）
13:50 - 16:50

Prof. Dr. Thomas Brock 教授
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涂料的化学与工艺的未来：需求与解答 / 新性能

主题论文 KEY NOTE 8

The Future of Coatings Chemistry & Processes: Needs & Answers / New Performances

涂料开发与应用的趋势主要由以下因素主导和控制：立法 / 溶剂含量降低的需求；扩大水性和粉末涂料、高固体分涂料、紫外光固化涂料和静电喷涂施工等应用前景；更快、更低成本的干燥 / 硬化工艺需求；成本降低的需求；新型创新性材料，特别是新型基料、颜料和填料；对表面结构和效果、表面清洁、表面耐久、节能等的新需求；纳米技术：层、结构和纳米颗粒；具有新要求的基材。

背景资料和参考文献显示有关减少溶剂含量类型涂料的技术现状和市场情况、特征性能、优点和局限性、应用领域以及对具有前景的干燥和固化方法的需求。

本文主要阐述高固体分涂料、水性和粉末涂料等涂料类型，并将讨论应用改善和新工艺领域的进展。同时对辐射固化领域包括 UV LED 固化和光子近红外固化新近的变化和扩张展开讨论。

Trends in paint development and application are dominated and controlled by: legislation / need for solvent reduction, expanding perspectives for water-borne and powder coatings, high solids, UV curing and electrostatic application etc., demand for faster and cheaper drying/hardening, need for cost reduction, new and innovative materials, especially new binder agents, pigments and fillers, examples of new demands on surface structures and effects, clean surfaces, resistant surfaces, energy saving, nano technology: layers, structures and panicles, new substrates with new requirements.

The referate shows the state of the art and the market situation regarding the solvent-reduced paint types, their particular properties, their advantages and limitations, the application areas, and the need of prospective drying and curing methods.

The paper will focus on paint such as high solids, water-borne and powder coatings, while the development of applications and new products will be discussed. Further discussion will be on the recent development and change of radiation curing, e.g. UV LEDS and photonic NIR-curing.

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Prof. Hongbo Liang
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一种新型自修复涂料制备及其修复行为研究

论文 PAPER 9

Preparation & Self-healing Behaviors of a New Self-healable Coating

智慧自修复涂料是近年来涂料研究中一个热点话题。本文报告了一种新型的自修复聚氨酯的制备方法，即在紫外光固化聚氨酯主链中引入具热可逆性的 Diels-Alder（DA）结构，以实现紫外光固化体系大分子网路的可控可逆交联。采用升温 / 降温 / 恒温 FTIR、差示扫描量热法（DSC）和动态热机械分析（DMA）系统研究了基于 DA 结构的光固化聚氨酯体系的逆反应机理，结果表明 DA 结构的热可逆性具有良好的可重复能力，光固化涂层随之从高度交联的大分子网路经由 rDA 反应发生解交联而形成仍具一定模量的线性聚合物。固化漆膜具有优异的修复性能，在 120°C 加热 10min 可以修复大约 100μm 的划痕。

Smart self-healable coating is a hot topic in recent years. In this paper, a new kind of self-healable polyurethane will be discussed, in which the Diels-Alder (DA) structure is introduced to the main chain of UV curable polyurethane, in order to realize the controllable reversible crosslinking of the UV curable system. FTIR with increasing/decreasing/constant temperature, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were conducted to study the thermal reversible mechanism of UV cured polyurethane coatings. The results indicate the thermal reversibility of DA structure is well-repeatable among the UV crosslinked networks. As a result, the highly cross-linked macromolecular network may decrosslink via rDA reaction under the action of heat and turn to a linear polymer with a certain modulus. The UV cured films show perfect self-healing properties and the scratch about 100μm can be healed within 10 min being heated under 120°C.

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基于点击化学的结构型抗菌水性聚氨酯合成与表征

论文 PAPER 10

Synthesis & Characterization of Structural Anti-bacterial Waterborne Polyurethane via Click Chemistry

以聚己内酯 1000（PCL1000）、异佛尔酮二异氰酸酯（IPDI）、2,2- 双（溴甲基）-1,3- 丙二醇、叠氮化钠（NaN_3）等为原料合成了带有叠氮基团的聚氨酯预聚体，以 1,1,3,3- 四甲基胍（TMG）、3- 溴丙炔合成了含炔基的五取代胍（TMG-AI），随后以点击反应为连接策略制备结构型抗菌水性聚氨酯分散体。采用红外光谱（FT-IR）、核磁共振波谱（NMR）表征了小分子单体的化学结构；通过抑菌圈实验验证了涂膜的接触型抗菌效果及非渗透特性，为接触型抗菌领域的研究提供了一种新的合成方法。抗菌结果显示，当水性聚氨酯中引入 TMG-AI 约为 5wt% 时，抗菌聚氨酯可对革兰氏阴性菌（大肠杆菌）及革兰氏阳性菌（金黄色葡萄球菌）产生显著的杀灭效果，抗菌率均达 99.9%。

In the paper, dihydroxy monomer with azide groups was synthesized with the reaction of 2-2-double bromine (meth)-1,3-propanediol and sodium azide (NaN_3). Using the dihydroxy monomer, polycaprolactone, isophorone diisocyanate, 1,4-butanediol, dimethylolpropionic acid as raw materials, waterborne polyurethane dispersion containing azide groups (WPU-N_3) was prepared. A functional guandine monomer containing alkyne (TMG-AI) was synthesize with the reaction of 1,1,3,3-tetramethyl guanidine and 3-bromine propiolic. By triggering the click reaction of azide groups in WPU-N_3 and alkyne groups in TMG-AI, a novel structural anti-bacterial waterborne polyurethane dispersion was prepared. The chemical structure of small molecular monomers was characterized by Fourier transform infrared spectroscope (FT-IR) and nuclear magnetic resonance spectrum(NMR). It was verified the bacterial contact-killing effects and non-penetration activity through the bacteriostatic ring experiment test. The results showed that the antibacterial effect for gram negative bacterial (E.coli) and gram positive bacterial (S.aureus) was significant, the antibacterial rate for both bacterial reached above 99.9% as the amount of TMG-AI in WPU about 5wt%.