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FULL LENGTH ARTICLE

Synthesis and evaluation of new anti-microbial additive based on pyrimidine derivative incorporated physically into polyurethane varnish for surface coating and into printing ink paste

H. Abd El-Wahab [a,*], Tamer S. Saleh [b], Ehab M. Zayed [b], A.S. El-Sayed [a], Ramy S.A. Assaker [c]

[a] *Chemistry Department, Faculty of Science, Al Azhar University, Nasr City 11884, Cairo, Egypt*
[b] *Department of Green Chemistry, National Research Centre, Dokki, Cairo 12622, Egypt*
[c] *Department of Forgery and Counterfeiting Research, Forensic Medicine Authority, Ministry of Justice, El-Sayeda Zeinab, 11461 Cairo, Egypt*

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Abstract In this study, heterocyclic compounds containing 3-((4-bromophenyl)diazenyl)-5-(methyl thio)-6-(phenylsulfonyl)pyrazolo-[1,5-a]pyrimidine-2,7-diamine (compound II) and 4-(methylthio)-3-phenylsulfonyl)benzo[4,5]imidazo[1,2-a]pyrimidin-2-amine (compound III) were prepared and their chemical structures were confirmed by spectral data. The new compounds were screened for antimicrobial activity against six different microbial strains when physically incorporated into polyurethane varnish formula and printing ink paste. Experimental coatings were manufactured on laboratory scale and applied by brush onto glass and steel panels. Results of the biological activity indicated that polyurethane varnishes and printing ink paste containing compounds II and III exhibit a very good antimicrobial effect. The physical and mechanical resistances of the polyurethane varnish formulations were also studied to evaluate any drawbacks associated with this addition. The studies revealed that the physical incorporation of compounds II and III enhances slightly the physical and mechanical properties.

1. Introduction

Pyrazole, pyramidine, phenylsulfone and their derivative products are some of the oldest and best known classes of nitrogen and sulfur containing compounds. In recent years there has been considerable interest in the phenylsulfonyl pyrazol

* Corresponding author.
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derivatives, which incorporated three important pharmacophore groups the phenylsulfonyl ring, pyrazol and pyrimidine heterocycles and the amine group. They have been reported to exhibit significant biological activities and are widely used as pharmaceuticals. They are capable of imparting antimicrobial activity properties when incorporated into polymers and their composites [1–2]. Biocide additives have been used to prolong the life of surface coatings. They prevent or slow down the growth of organisms on the surface coating. Without biocide additives, the biological species start to adhere on the coating surface and lead to disbonding and blistering of coatings under various service conditions. Biocides in paint fall into two main categories; those used for wet state protection and those for film protection. Wet state (in-can) biocides may be bactericides and fungicides, which were used to protect the coating material until it can be applied. Film biocides, which can be fungicide or algaecides, are incorporated to prevent the growth of fungi and algae on applied surface coatings [3–5]. Sharif Ahmad et al. have successfully used it as a starting material for the development of polyetheramides, polyesteramides, polyesteramide urethanes and polyamide urethanes, which find application as protective coating materials and can be used as an effective antibacterial and biologically safe corrosion protective material [6–11]. In 1937 the birth of polyurethanes (PUs) occurred in Germany when Bayer laboratories explored their use as fiber-forming polymers [12]. Polyurethanes are an important and very versatile class of polymer materials with desirable properties, such as high abrasion resistance, tear strength, excellent shock absorption, flexibility and elasticity [13–15]. The attractiveness of polyurethanes stems from their excellent bonding to different substrates, relatively low price and fast reaction time [16]. Polyurethane top-coats, recommended for paint systems commonly utilized for corrosion protection of steel structures, are used in highly corrosive atmospheres (C5 category) [17]. Polyurethane, polyester and polyesteramide are susceptible to microbial attack, when they are exposed to the atmosphere or used as an adhesive or a coating material. Generally microorganisms have been found to cause disbonding and blistering of coatings under various service conditions [18–20]. Marine biofouling is a natural phenomenon representing one of the greatest problems in marine technology and navigation, since the accumulation of organisms such as barnacle, tube worms and algae on the submerged surfaces of the vessels results in important speed reduction and considerably higher fuel consumption. To circumvent these problems, antifouling paints, i.e. paint formulations traditionally containing biocidal species, are used to protect the submerged surfaces from marine biofouling [21]. Till the end of 1990s, the most effective antifouling paints were based on organotin compounds, mostly tributyltin compounds (TBT-based paints). TBT and its derivatives were found to be harmful molecules to marine ecosystems by Alzieu [22]. And so it is completely prohibited by 1 January 2008 [23–25]. This short-dated restriction promotes research for new ecological paints. One of the methods to overcome such a problem is to develop polymers having biocidal activities [26]. A large number of naturally occurring compounds contain heterocyclic rings as an important part of their structure such as coumarin (IUPAC name: *2H*-Chromen-2-one) compounds and its derivatives are used as medicines [27]. Coumarin compounds and their derivatives form a group of more than 40 drugs, which are widely used in medicine as anticoagulant, hypertensive, antiarrhythmic, and immunomodulant agents [28] and possess remarkable activities against bacteria [29] and fungi [30]. Furthermore, pyrimidine derivatives having various substituted thiazole rings at carbon-3 exhibit promising biological activities [31]. Heterocyclic compounds based on sulfur have attracted continuing interest because of their varied biological activities [32], which have found applications in the treatment of microbial infections [33–34]. Thiazole and pyrazol are parent materials for various chemical compounds including sulfur drugs, biocides, fungicides, dyes, and chemical reaction accelerators. In addition, 2-amino thiazole derivatives are reported to exhibit significant biological activities and are widely used as pharmaceuticals [35]. On the basis of all of this evidence, this study reports the synthesis, characterization and antimicrobial activities of new structure hybrids incorporating the phenylsulfone and pyrazol ring system. This combination was anticipated to influence on the biological activities. The heterocyclic compound based on phenylsulfonyl moiety 3,3-bis(methylethio)-2-(phenylperoxythio)acrylonitrile, 3-((4-bromophenyl)diazenyl)-5-(methylthio)-6-(phenylsulfonyl)pyrazolo-[1,5-a]pyrimidine-2,7-diamine and 4-(methylthio)-3-(phenylsulfonyl)benzo[4,5]imidazo[1,2-a]pyrimidin-2-amine were physically added to the polyurethane varnish and printing ink paste, to make it antimicrobial. The biological activity test was used to assess the biological activity of the additive. The physical and mechanical resistances were also studied to evaluate any drawbacks associated with the additive.

2. Experimental

2.1. Materials

All chemicals used during this study were sourced either internationally, or from local companies, and are of pure grade.

Sodium benzenesulfinate, 2-chloroacetonitrile and dimethylformamide were purchased from *Aldrich Chemical Co*.

Carbon disulfide was purchased from *Merck Co., Germany*.

Methyl iodide was purchased from *British Drug Houses* (*BDH*).

Ethanol and potassium hydroxide were purchased from El-Nasr Pharmaceutical and Chemical Co. (ADWIC), EGYPT.

Aniline and its substituted derivatives, hydrazine hydrate and pyridine were purchased from *Aldrich Chemical Co*.

Malononitrile and piperidine were purchased from *Across Organics Co*. (*Belgium*).

Hydrochloric acid and sodium nitrite were purchased from *El-Nasr Pharmaceutical and Chemical Co*. (*ADWIC*), *EGYPT*.

2-Aminobenzimidazole was purchased from *Merck Co., Germany*.

2.2. Methods and techniques

New anti-microbial additives based on pyrimidine derivative (compounds II & III) were prepared as presented in Scheme 1.

2.2.1. Synthesis of 3,3-bis(methylthio)-2-(phenylperoxythio)-acrylonitrile as starting material (compound I)

A solution of 2-(phenylsulfonyl) acetonitrile (0.01 mol) and sodium ethoxide (0.46 g, 0.02 mol) in 20 ml absolute ethanol was refluxed for 20 min, after cooling; carbon disulfide