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Preparation of polyurethane coating formulation based on dihydropyridine derivatives as an insecticide and antifungal additives for surface coating applications

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Abstract Pyridine derivatives are prepared and evaluated before being incorporated into polyurethane coating formulations to create antifungal and insecticidal coating compositions. Different analyses, including Fourier transform infrared (FTIR), mass, proton nuclear magnetic resonance (^{1}HNMR), and carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra, were used to confirm the synthesized compounds. The material has been coated using a polyurethane coating mixture. Gloss, scratch resistance, flexibility, and adhesion are some of the coating attributes investigated; mechanical capabilities include impact resistance and shore hardness, and physicochemical properties such as chemical resistance of coated polyurethane (PU) samples are also investigated. PU coatings were applied to substrates to measure coating properties. The mechanical properties of the PU cast films were measured. The results of the experiments revealed that all PU coatings based on dihydropyridine derivatives had good scratch resistance which varied from > 1.5 to > 2 kg. While reducing gloss value varied from 65 to 85, there is no effect of the prepared compounds in the other mechanical test. These PU coatings have excellent chemical resistance except the alkali resistance as evidenced by their physicochemical properties. The observed antifungal and insecticide activities indicated that dry wood coated with PU based on dihydropyridine derivatives is promising for resistance to these insects and fungi, in comparison with the paint as blank. The results revealed that the inhibition zones diameter by compound 2 were 25.1 ± 0.69, 23.2 ± 0.94, 20.16 ± 0.62, 20 ± 0.80, and 18 ± 0.81 mm against *A. terreus, A. niger, A. flavus*, *C. albicans*, and *A. fumigatus*, respectively, whereas the inhibition zones (IZ) diameter by compound 3 were 22.56 ± 0.30, 21.03 ± 0.49, 21.03 ± 0.61, 21 ± 0.66, and 20 ± 0.78 mm versus *A. niger, A. fumigatus A. flavus*, *C. albicans*, and *A. terreus*, respectively. The ordering activity against insects increased as the dose concentration of the pyridine derivatives was increased.

Keywords Antifungal, Insecticide coating, Polyurethane coating, Pyridine derivatives

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Introduction

The insecticidal activity of paint and paint films is a significant issue that has recently received a lot of attention, and it became evident that there had been very little research done on the subject. Indoor insect control with a pigmented water-base coating containing 0.1–2 percent chlorpyrifos or pyrethrin was found to be both safe and effective.[1,2] Insecticidal paints have been on the market for several years, particularly in Europe and North America, where they are sold as a pest repellant for walls and ceilings. Although insecticidal paints have been proposed for disease vector control since the 1940s, they have received little attention in comparison with indoor residual spraying, which has the same basic mechanism of action.[3] The

widespread use of insecticides may be contributing to global insect reduction.[4] An effective alternative to using environmentally friendly essential oils and plant extracts in coatings to repel insects from buildings is to use environmentally friendly essential oils and plant extracts in coatings.[5] Insecticidal paints have been on the market for a number of years, especially in Europe and North America, where they are advertised as a pest repellant for vermin living on walls and ceilings.[6,7] The amount of pesticide that is efficiently delivered to the target insect is determined by the type of coating formulation and substrate, as well as the size and adhesion qualities of insecticidal particles on these substrates.[8] Mosquitoes and other small flying insects are notoriously difficult to eradicate with lethal pesticide doses. Current vector-control technologies use oil or water-based coating formulations as carriers to achieve chemical adherence and retention on vertical surfaces such as walls or netting.[9] When insects land, crawl, or climb on coatings, they interact with them. Many insects are classified as pests because they pose a threat to agriculture, forestry, infrastructure, and human health. Controlling insect infestations can be done with insecticides, insect repellents, and coatings with poor insect adherence.[10–13] Insect pests can further infest, or damage objects or furniture made of wood, wool, linen, etc., as well as pieces of art or books if they enter museums or libraries.[14] Insecticides in building interior and exterior coatings (housing, hospitals, restaurants, etc.) can be effective at repelling, killing, or preventing the presence of insects.[15–17] Essential oils repel and kill insects when blended into a coating, and encapsulation allows for a delayed release of active components.[18] When a standard paint formulation is combined with an active ingredient known as an insect repellent or killer during paint production, it has proven to be an effective preventive measure against flying and crawling insects when applied to walls.[19,20] The pulse beetle was used to test the insecticidal activity of isoxazole derivatives that had been synthesized and characterized. The synthesized compounds outperformed the organophosphorus pesticide that was prescribed.[21] Insects find flu on-coated walls extremely slippery, as aggregates of PTFE particles detach from the surfaces and adhere to their pads. Climbing ants, on the other hand, can remove Fluon coatings from the walls of their nest containers (A.F. & W.F., personal observation), and the coatings are significantly less slippery in high humidity conditions.[22] New insecticide agents based on isoxazole benzenesulfonamide derivatives were investigated, and their incorporation into waterborne household paint formulations as environmentally friendly paints, as well as the evaluation of their physical, mechanical, biological, and insecticide activity, was carried out.[23] The aesthetic and protective properties of an insecticide-based coating developed were studied. The components used in the manufacture of the paints, in addition to the insecticides X (deltamethrin), Y (cypermethrin), and Z (disclorvos), are common basic materials in the paint formulation.[24] Resistance to insecticides is a severe and growing concern to malaria and other mosquito-borne diseases control. As a result, researchers researched and published a novel insecticide application approach based on netting coated with an electrostatic coating that binds insecticidal particles via polarity.[25] The effect of CuO nanoparticles on the antifungal activity of polyurethane/CuO coating film was studied. The antifungal activity of polyurethane/CuO coating film against one type of fungus (penicillium) was measured by the disk diffusion method and the optimum conditions were determined.[26] A series of polyurethane (PU) membranes modified by zinc oxide nanoparticles was prepared. A very widespread aggressive fungal species represented by *Aspergillus brasiliensis* has been used as a biological material. The results suggest that the polyurethane membranes modified by nano-ZnO have important antifungal properties and can be used in biomedical applications.[27] Evaluation of the activity of four commercial TiO_2-based paints under natural indoor light against selected microscopic fungi was reported. A wide variety of fungal isolation sources reflected potential applications of the TiO_2-based photocatalytic reaction for disinfection of plant materials and biosolids and for improvement in hygienic conditions in plant storage and organic waste treatment facilities.[28–30] Polyurethane-Based Coatings with Promising Antibacterial Properties. PU-based coatings and films were successfully prepared and investigated.[31] The preparation of novel antimicrobial coating materials based on polyethyleneimine (PEI) and study of their structure − activity relationship and the mechanism of action at the molecular level.[32] The effectiveness of these polymers as the antimicrobial coating was also evaluated along with the conventional polymers and commercial paint. Hemocompatibility of the polymeric coating was also evaluated with human erythrocytes.[33] Antimicrobial coatings based on newly incorporated alkyd, waterborne paints, and polyurethane, as well as new modified polyester amide resins as varnishes, either based on synthesized heterocyclic compounds or prepared metal complexes as antimicrobial agents for surface coating applications, were studied and reported.[34–37] In this study, we focused on developing new insecticide and antifungal agents based on pyridine derivatives (**2** and **3** derivatives) and incorporating them into polyurethane varnish formulations to assess their biological and insecticide activity as well as physical and mechanical properties after incorporation.

Materials and methods

Materials

All the chemicals used during the study reported here were either obtained locally or from global firms. They were all high purity and used without further purifica-

tion. These, including 2-bromobenzaldehyde, malononitrile, dioxane, salicylaldehyde, and piperidine, were obtained from El Nasr Pharmaceutical Company, Egypt. PU varnish was supplied from Pachin Paint Company of chemical and paints.

Methods and technique

Schiff base **1** as a key intermediate was constructed according to the method prescribed in the literature[34] by stirring equimolar amounts of 2-cyanoacetate hydrazide[35] with o-bromobenzaldehyde in 50 mL absolute ethanol with 1 mL of glacial acetic acid as catalyst (Scheme 1). The condensation reaction of *N*'-(2-bromobenzylidene)-2-cyanoacetohydrazide **1** with malononitrile in refluxing absolute ethanol and 3 drops of piperidine as catalyst led to the formation of starting material 1,6-diamino-4-(2-bromophenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile as a good product (Scheme 1).

6-Diamino-4-(2-bromophenyl)-2-oxo-1, 2-dihydropyridine-3,5-dicarbonitrile (2)

A mixture of *N*'-(2-bromobenzylidene)-2-cyanoacetohydrazide **1**[34] (2.66 g, 0.01 mol) and malononitrile (0.66 mL, 0.01 mol) in absolute ethanol (20 mL) containing two drops of piperidine was refluxed for 5 h. The pale brown precipitate obtained during heating was filtered off and recrystallized from suitable solvents to give compound **2** as brown crystals; yield (2.31 g, 70%); m.p. 170ºC.

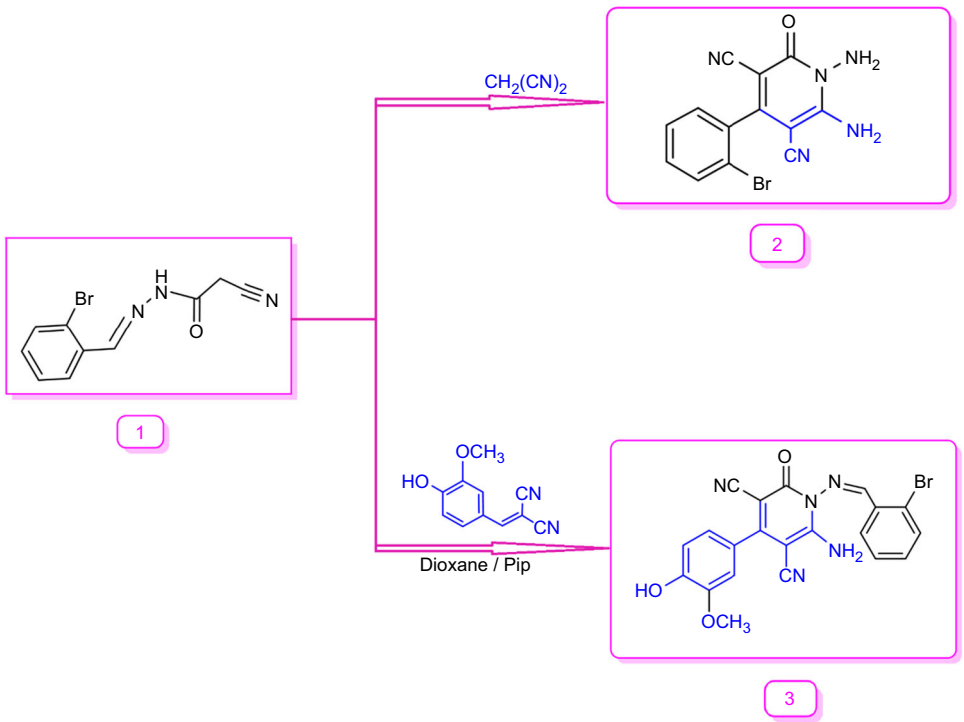
6-Amino-1-((2-bromobenzylidene)amino)-4-(4-hydroxy-3-methoxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (3)

To a mixture of **1** (2.66 g, 0.01 mol) and 2-(4-hydroxy-3-methoxybenzylidene)malononitrile (2 g, 0.01 mol) and 1 mL of Pepperdine was refluxed in 30 mL of 1,4-dioxane for 6 h then left to evaporate. The residue solid product was washed with ethanol and then the solid was collected by filtration and recrystallized from ethanol to give compounds **3** as orange powder; (3.24 g, 70%) m.p, 160ºC. Melting points of the reaction products were determined in open capillary tubes on an electrothermal melting point apparatus and were uncorrected. The structure of compound **2** was proved based on analytical and spectral data (Scheme 2).

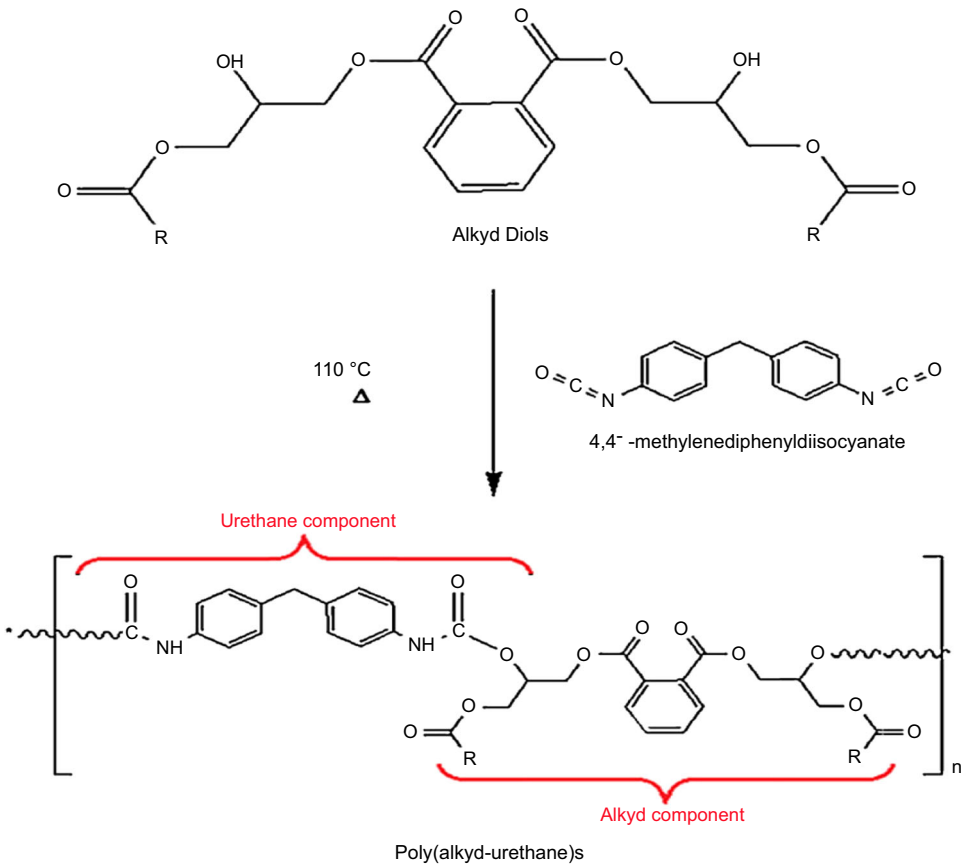
Characterization of the prepared organic compound by spectral analysis

The FTIR measurements were recorded on PerkinElmer Model 297 IR spectrometer using the KBr wafer technique at the Central Laboratory of the Faculty of Science, Cairo University.

The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Varian Gemini spectrometer



Scheme 1: Formation of 1,6-diaminopyridone[2] and 1,2-dihydropyridine-3,5-dicarbonitrile[3]



Scheme 2: Suggested structure of urethanated alkyd

with chemical shift (δ) expressed in ppm downfield using tetramethyl lane (TMS) as an internal standard at the main Defense Chemical Laboratory.

Mass spectra were conducted using Shimadzu GC-MSQP 1000 EX instrument operating at 70 eV and the elemental analyses were performed on a PerkinElmer 2400 CHN elemental analyzer at the Microanalytical Center of Al-Azhar University.

All reactions were monitored by TLC and PTLC (1-mm layer thickness), which were conducted using pre-coated plates of silica gel 60 F254 (Merck), and spots were detected using a UV lamp (254 nm). The spots on TLC were visualized by warming with 5% cerium ammonium molybdate in 2 N H_2SO_4 sprayed plates on hot plate.

Polyurethane coating fabrication

The coating formulations (Table 1) were made by adding dihydropyridine derivatives into polyurethane varnish in a ratio of 1.0 weight percent. The dihydropyridine derivatives were dispersed and aligned in the PU (polyurethane) using a combination of high-speed disk (HSD) and ultrasonication dispersion techniques. HSD dispersers (high-speed impellers) with a rotation speed of 4000 rpm were first used for 30 min to break down the particles by providing shear stress during the high-speed rotation. Dihydropyridine derivatives solutions were added to the PU varnish and were subjected to ultrasonication with a total duration of 60 min to ensure the proper dispersion of the dihydropyridine derivatives in the varnish matrix. Following the dispersion, the resin was mechanically mixed with the dihydropyridine derivatives for another 10 min. Table 1 shows the chemical components of the developed PU coating.[23] The glass and wood panels were cleaned with acetone before the coatings were applied. Single-layer coatings were applied and cured at room temperature. After 24 h all the coated samples could completely dry and be ready to do all the mechanical tests. The thickness of dried coating films was measured with a Glucometer 415 thickness gauge, and the tested samples had an average thickness of 60 5 m. ASTM Method D:1005–13.

We have chosen the PU varnish because of many factors. In addition in this research, the main aim is for insecticide and fungal resistance, so we are concerned to choose the type of varnish that is suitable for wood surface which is subjected to the insects and fungi. So we choose it for these reasons, Mold, Mildew and Fungus Resistance, Strong Bonding Properties, Performance in Harsh Environments, Resistance to Water, Oil and Grease. Once dry, polyurethane pro-

Table 1: Formulation of two pack high gloss polyurethane varnish incorporated with dihydropyridine derivatives

No	Materials	Weight (g)
Composition of part 1(polyol)		
1	Butyl acetate	10.0
2	Toluene	6.0
3	Cyclohexanone	5.2
4	Nitro cellulose soln 3/4 second	12.0
5	Short oil alkyd (COCX 35–97) 70%	34.1
6	Wax solution	27.9
7	Acematt ok (412) matting agent	2.3
8	BYK leveling agent	0.3
9	Prepared organic compounds (dihydropyridine derivatives)	1–2
	Total	100
Composition of part 2 (hardener)		
9	Butyl acetate ''urethane grade''	68,0
10	Desmodur''IL 351''	24.0
11	Desmodur L (75)	8.0
	Total	100

Desmodur''IL 351: aromatic polyisocyanate based on toluene diisocyanate. It is suitable for use as the hardener component for fast-drying., Desmodur L 75 is an aromatic polyisocyanate based on toluene diisocyanate (TDI). It can be used in combination with various Desmophen®, Baycoll®

duces the hardest, most durable finish in the wood-finishing industry, and water-based polyurethane is used outside for any outdoor furniture, decks, or floors. However, more resistance to atmospheric agents has a greater surface hardness, able to guarantee better adhesion on the substrate. Because of these characteristics, they are the most used for wood treatment.

Application of the Insecticide-based PU (polyurethane) varnish and Control PU (polyurethane) varnish

The insecticide-based and control paints were thoroughly mixed to achieve the desired homogeneity. The 16 experimental boxes of size 2×2 in.^{2} built for this investigation had two coats of these paints applied with a 1 in. brush. The painted boxes were allowed to cure until the surface was clean and smooth, the boxes were kept upright and flat on the floor at room temperature.[24,38]

Characterization techniques

Film casting and testing

The panels substrate was prepared according to ASTM Method D609-17, and the coating film dry film thickness (DFT) was measured according to ASTM Method D1005-13. A specular gloss of coated films was measured using a Sheen, UK gloss meter according to ASTM Method D523-18. Scratch hardness was measured per STM D5178-98, 2008. Adhesion was measured by using a Sheen, UK cross-cut adhesion tester according to ASTM Method D3359-17. The flexibility (bend) test was measured by a Mandrel bend tester from Sheen UK, according to ASTM Method D522-17. Resistance to mechanical damage is ''impact resistance'' (ASTM G14-04(2018). The chemical resistance test was accomplished according to ASTM C267-20 1.9.2020.

Scanning electron microscopy (SEM)

Scanning electron microscope (SEM), the surface morphology of the PU coating formulation, was observed with the help of a scanning electron microscope (Joel JSM 6360LA, Japan) at an accelerated voltage of 10 kV. The fracture surfaces were vacuum coated with gold for scanning electron microscope (SEM).

Antifungal activity of pyridine derivatives (2 and 3)

Antifungal activity of **2** and **3** derivatives was performed toward *Aspergillus terreus, A. niger, A. flavus, A. fumigatus and C. albicans* using agar well diffusion assay.[5,39,40] Fungal strains were initially grown on PDA plates and incubated at 30°C for 2–4 days. The fungal suspension was prepared in sterilized buffer solution pH 7.0, and then, the inoculum was adjusted to 10^6 spores/mL. One mL was uniformly distributed on agar PDA plates. Two-handed (200) μL of each **2** and **3** derivatives were put in agar wells (6 mm) then incubated at 30°C. After 48 h of incubation, the inhibition

zone diameter was measured. The paint was used as a reference control.

Characterization of insects

Insect rearing

Laboratory reared colony of *Musca domestica* (House Fly) free from insecticides and pathogens, obtained from animal house, Flies Research Laboratory, animal house, Faculty of science, Al-Azhar University in Cairo, was maintained starting from egg rafts.[38]

Bioassay test

The bioassay was used for laboratory tests of the **2** and **3** insecticidal efficacies against adults of *M. domestica* according to (Levchenko et al.) with slight modification. Flies were starved for 12 h before the tests. Acetone solutions of insecticides (0.3 mL) were used to soak the sugar cube (5.5 g), and in the control test, the sugar was treated with pure acetone in the same volume. Derivatives **2** and **3** were tested at concentrations from 10 to 30 ppm. Hence, two stock solutions were chosen for each insecticide (10, 15, 20, 25 and 30 ppm for **2** and **3**). After the acetone evaporated, the sugar was placed in glass cups with starved flies (from 15 to 25). The cups were sealed with mesh pistons from the top and supplied with water drinkers. The mortality of the flies was recorded after 24, 48 and 72 h. Each concentration was tested at least 3 times, and the tests were carried out on different days.[41]

Bioassay with paint

Flies were exposed to treated panels by anesthetizing them with carbon dioxide and transferring 25 flies to each panel. Flies were confined to panels by placing wooden embroidery hoops (14.5 cm inner diameter, 1 cm thick) that had been covered with coarse mesh screen cloth (14 squares per cm^2). Prior to fly transfer, a strip of duct tape 23 cm × 9 cm) was affixed near the bottom of the hoop for the duration of the exposure and this prevented fly contact with the treated panel while the insects were anesthetized or immobilized. Hoops were secured to the plywood panels with two rubber bands stretched across the hoop and fastened to push pins. After the hoop was secured, panels were hung vertically for a 6-h holding period at 25°C under constant fluorescent lighting. This design was an attempt to replicate the conditions presented to flies in dairies, including the choice of resting on a treated surface or moving to untreated areas. Throughout the holding period, flies were observed walking on the surface of the panels.[24] Following exposure on the panels, flies were again anesthetized and transferred to 118-mL plastic cups with screened lids. Flies were provided a dental wick soaked in 10% sugar water and held at 25°C under constant fluorescent lighting. Mortality was assessed after 48 h, and flies were considered dead if they were ataxic. The assays were replicated three times 275 insects per replication), with three panels per farm 2including the CS strain) and insecticide at each replication. For all studies, we calculated the percentage mortality and corrected the data for control mortality.[42] To normalize the data, prior to statistical analysis a log $2x + 0.5$ transformation was performed; however, non-transformed data are presented in the figures. Data from each chemical examined were examined using a multi-factorial analysis of variance.[43] The statistical model contained the fixed effects of study replication, panel treatment, fly strain, within-study replication and three interaction terms: study * panel treatment, a study *fly strain, and panel treatment *fly strain. Data within each chemical were tested for treatment differences using Tukey's mean separation.

Statistical analysis of data

SPSS software package 16.0 version was used for all analyses. For both insect species, acute toxicity data from laboratory assays were transformed into arcsine/proportion values and then analyzed using a two-way ANOVA with two factors (i.e., dosage and mosquito instar). Means were separated by Tukey's HSD test. Furthermore, insect pest mortality data from laboratory assays were analyzed by probit analysis, calculating LC_{50} and LC_{90} following the method by Finney.[25]

Result and discussion

Thus, IR spectrum of compound **2** showed a characteristic absorption band at 3407, 3313, 3210 cm^{-1} due to two bands of amino groups (2 NH_2), 2207, 1676 cm^{-1} for two cyano groups (2 $C \equiv N$) and a carbonyl group (C=O), respectively (Fig. S1). Also, the ^1H NMR spectrum of compound **2** revealed the presence of two singlets signal that was exchangeable with D_2O at δ 5.70 and 8.60 ppm because of the presence of two amino groups (Figs. S2 and S3). In addition, the ^{13}C NMR spectrum showed characteristic signals at 166.93 ppm assigned to (C=O) and 116.01 ppm, 116.41 ppm for two cyano groups in addition to signals at 75.40 (C^5 pyridine), 114.59 (C^3 pyridine), 120.81, 124.68, 128.73, 130.54, 132.14, 134.27, 136.31 (7C- aromatic carbons), 159.27, 159.48 (2C-NH_2) (Fig. S4). Compound 5 further indicated from its mass spectrum the molecular ion peak at m/z 330, which is in accordance with the molecular formula $C_{13}H_8BrN_5O$. Treating **2** with 2-(4-hydroxy-3-methoxybenzylidene)malononitrile in dioxane containing two drops piperidine gave 6-amino-1-((2-bromobenzylidene)amino)-4-(4-hydroxy-3-methoxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile 3 (Scheme 1). The reaction could start with a nucleophilic addition to the

active double bond, then a cycloaddition of the amino group,[44, 45] and finally with concomitant dehydration to produce **3** based on elemental analysis and spectral data. IR spectrum of **3** revealed distinguishing characteristic absorption bands at 3404, 3192 cm^{-1} due to bands of the amino group (NH_2) and hydroxyl group (OH), 2213 cm^{-1} for cyano groups (C ≡ N) and presence of absorption bands at 1654 cm^{-1} capable of being assigned carbonyl group (C=O) (Fig. S5). The ^{1}H NMR spectrum of compound **3** showed singlet signals at 3.15 ppm attributed to methoxy protons and because of the presence of an amino group and hydroxyl group, there was a presence of a single signal that was exchangeable with D_2O at 5.38 and 12.00 ppm, respectively (Figs. S6 and S7). In addition to the presence of multiplet signals in the region at d 6.90—8.53 ppm corresponding to the aromatic protons. Furthermore, its ^{13}C NMR spectrum exhibited three signals a 116.16, 117.04 ppm assigned to (C ≡ N) and 159.77, 169.14 ppm assigned to (CH=N) and (C=O), respectively. In addition, signals at 114.71, 114.38, 126.92, 127.83, 128.02, 128.49, 128.73, 129.04, 130.27, 130.61, 132.26, 132.53, 133.87, and 157.09 ppm corresponded to other carbon atoms and aromatic carbons, which is in accordance with the molecular formula $C_{21}H_{14}BrN_5O_3$ (Fig. S8).

Characterization of the prepared polyurethane varnish embedded with pyridine derivatives as antifungal and insecticide agents

FTIR analysis of pure PU varnish

Figure 1 indicates the mid-IR spectrum of pure PU to analyze its adsorption functional groups. The major adsorption peak generated around 3400 cm^{-1} is owing to the stretching vibration of the terminal OH group, while the band obtained around 1300 cm^{-1} can be due to the OH bending vibrations. The other peaks observed around 2900 and 3000 cm^{-1} could be attributed to aliphatic and aromatic C–H, respectively. The band around 1750 cm^{-1} corresponds to the carbonyl of the carbamate group (polyurethane linkage).

SEM observation

The scanning electron microscopy (SEM) was adequately performed to observe the morphology of the net PU varnish and PU incorporation with the prepared insecticide and antifungal additives. The SEM images of samples are shown in Fig. 2.

As shown in Fig. 2a, it is clearly seen that the SEM image of net polyurethane varnish formed a relatively smooth surface. Meanwhile, the surface morphology of raw polyurethane incorporated with compounds **2** and **3** (Fig. 2b, c) exhibits an obvious biphase character. The integrated polyurethane with compounds **2** and **3** had a smooth and uniform surface, which could have been due to the presence of hyperbranched. The introduction of branched BP on the surface of the prepared compounds (**2** and **3**) can significantly cause a significant decrease in agglomeration, and also may be due to the high dispersion of the prepared compounds **2** and **3** on the surface morphology of net polyurethane varnish.

Physical and mechanical characteristics of the coated films by PU (polyurethane) varnish embedded with the prepared additives

A Sheen UK gloss meter was used to quantify specular gloss. When seen at a 60° angle, the dihydropyridine derivatives additives reduced the gloss levels from 85

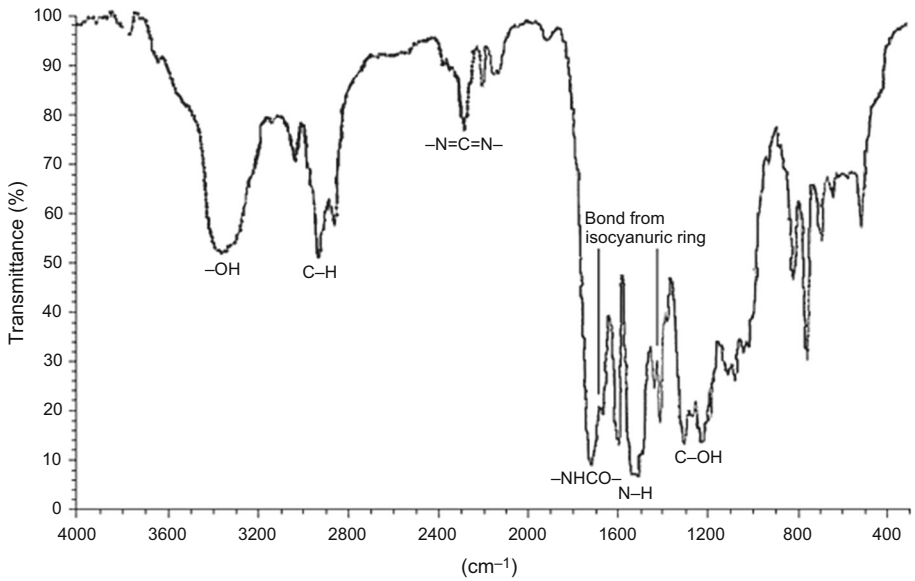


Fig. 1: FTIR spectroscopy of pure PU

to 65, as shown in Table 2. Although the percentage of dihydropyridine derivatives additives applied to the PU varnish recipe is about 1%, the results reveal that the dihydropyridine derivatives additives lowered gloss by modifying the volume connection between solid components and total film-forming ingredients. The coated films' gloss value is reduced by adding the solid component. The impact strength also decreased because they decreased the bulk elasticity of the paint. Sheen scratch tester was used to determine the scratch hardness (scratch resistance) that was increased by our additives to reach > 2 kg. Also, crosscut (crosshatch) mechanical adhesion of the modified polyurethane-based coatings was tested. Our coated steel and wood substrates showed no flaking and were classified as 5B. As a result, for good adhesion, the coated panels passed with good ratings the flexibility bend test that was conducted on a ¼ inch Mandrel bend tester supplied by Sheen, UK. Notably, all of the coating films have the same adhesion and flexibility, and the formula passed the test without cracking. As a result, the dihydropyridine derivatives (compounds **2** and **3**) additives improve the gloss and scratch hardness of the reformulated polyurethane-based coating. This improvement was attributed to the benzene ring and some function groups like NH_2 and CN in the prepared compounds while having no negative impact.[23,46] Also, based on the obtained results in Table 3, the actual data indicated that all prepared coated films by PU coating generally showed good resistance and were completely unaffected by the solvent and distilled water due to the good, crosslinked network and good

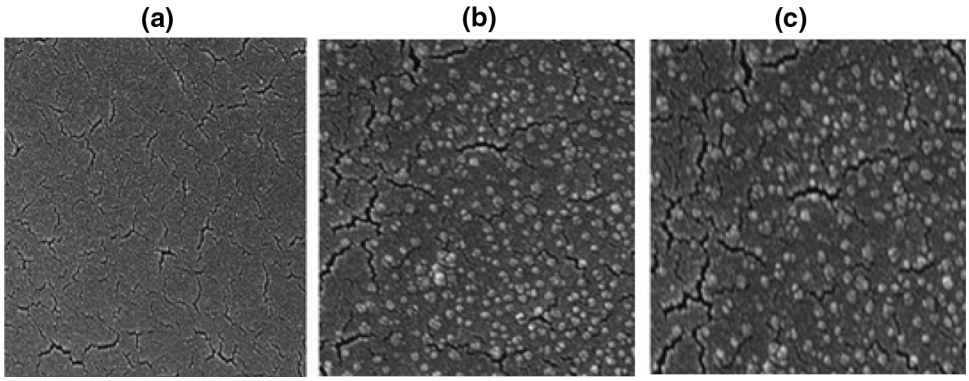


Fig. 2: SEM images of (a) net PU varnish, (b) incorporated PU with comp. 2, (c) incorporated PU with comp. 3

Table 2: Physical and mechanical characteristics of the coated films by PU varnish embedded with the prepared additives

Formulation	%	Dry film thickness (μm)	Gloss at 60° (GU)	Hardness (Kg)	Adhesion	Flexibility	Impact resistance (J)
Blank formulation (pure PU varnish)	–	55	85	> 1.5	5B	Pass	1.7
Blank polyurethane and comp. 2	1.0	60	75	> 2	5B	Pass	1.5
Blank polyurethane and comp. 3	1.0	60	65	> 2	5B	Pass	1.2

Table 3: Chemical resistance of pure PU varnish and PU incorporated with dihydropyridine derivatives

Formulation	%	Water	Acid	Alkali	Solvent
PU varnish (blank)	–	Unaffected	Unaffected	Affected	Unaffected
PU varnish and comp. 2	1	Unaffected	Unaffected	Affected	Unaffected
PU varnish and comp. 3	1	Unaffected	Unaffected	Affected	Unaffected

adhesion characteristics of PU varnish. However, the poor alkali resistance results of all dry coated films as shown in Table 3, may be due to the presence of alkali hydrolyzable ester linkages in the PU structure.[47]

Antifungal activity

Evaluation of the antifungal activity of 2 and 3 pyridine derivatives

The pyridine derivatives (**2** and **3**) generally showed good anti-fungal activity versus *C. albicans* (unicellular fungi) *A. terreus, A. niger, A. fumigatus* and *A. flavus* (multicellular fungi) are given in Figs. 3 and 4 in comparison with the paint as blank. Results revealed that the inhibition zones diameter by compound **2** were 25.1 ± 0.69, 23.2 ± 0.94, 20.16 ± 0.62, 20 ± 0.80, and 18 ± 0.81 mm against *A. terreus, A. niger, A. flavus, and C. albicans*, and *A. fumigatus*, respectively, whereas the inhibition zones (IZ) diameter by compound **3** were 22.56 ± 0.30, 21.03 ± 0.49, 21.03 ± 0.61, 21 ± 0.66, and 20 ± 0.78 mm versus *A. niger, A. fumigatus A. flavus*, *C. albicans*, and *A. terreus,*, respectively. In the end, it became clear from the results that the pyridine derivatives (compounds **2** and **3**) were effective on unicellular fungi (*C. albicans*) and multicellular fungi (*A. terreus, A. niger, A. fumigatus*, and *A. flavus)*. The antifungal action is attributed to a variety of reasons, including the fungus resistance of this type of varnish (polyurethane varnish),[48] which has been enhanced by the addition of pyridine derivatives. This growth and improvement could be attributable to the pyridine derivatives that contain two free NH_2 aromatics, two CN groups, a bromine atom, and a pyridine heterocyclic ring, as shown in compound **2**. The activity of compound **3** is due to the same causes as

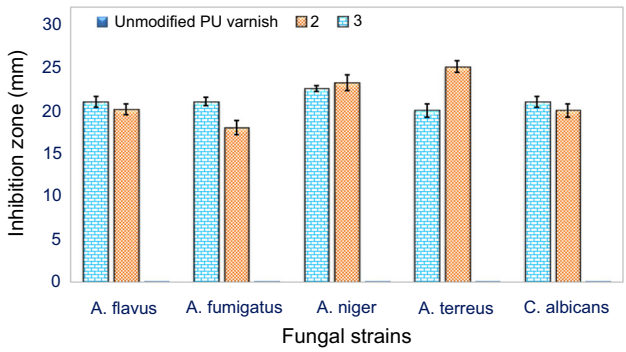


Fig. 3: Antifungal activity of the compounds 2 and 3 pyridine derivatives

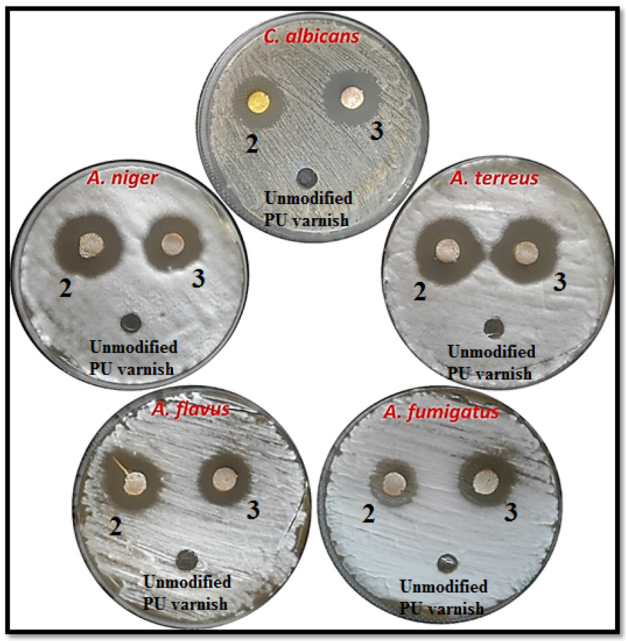


Fig. 4: Antifungal activity of the compounds 2 and 3 pyridine derivatives (Color figure online)

Table 4: Insecticide activity of 2 and 3 against adult house fly *Musca domestica* and calculated $LC_{50}(LC_{90})$ after 72 h of mortality

Insecticides	Comp 2			$LC_{50}(LC_{90})$	Comp 3			$LC_{50}(LC_{90})$
Concentrations (ppm)	24 h	48 h	72 h		24 h	48 h	72 h	
10	29.8 ± 1.2	41.7 ± 3.8	50.7 ± 4.4	33.04(59.47)	26.4 ± 0.9	47.6 ± 3.1	68.0 ± 3.7	51.85(91.33)
15	30.1 ± 1.6	44.5 ± 2.2	60.1 ± 3.1		31.8 ± 1.9	51.2 ± 2.0	72.4 ± 4.4	
20	32.8 ± 1.9	47.3 ± 4.1	71.3 ± 2.9		35.7 ± 1.4	62.6 ± 3.1	80.6 ± 1.7	
25	36.3 ± 1.1	50.6 ± 3.1	73.6 ± 0.9		38.8 ± 2.1	76.4 ± 2.7	83.8 ± 1.6	
30	42.8 ± 2.0	59.4 ± 2.1	89.5 ± 1.9		44.3 ± 1.1	79.1 ± 2.1	91.5 ± 1.2	

Table 5: Insecticide activity of 2 and 3 incorporated with PU varnish against adult of house fly *Musca domestica* and calculate $LC_{50}(LC_{90})$ after 72 h of mortality

Insecticides	PU varnish and comp. 2			$LC_{50}(LC_{90})$	PU varnish and comp. 3			$LC_{50}(LC_{90})$
Concentrations (ppm)	24 h	48 h	72 h		24 h	48 h	72 h	
10	22.56 ± 0.2	34.8 ± 2.4	40.1 ± 2.1	28.06(50.51)	23.9 ± 1.1	37.6 ± 1.6	58.3 ± 1.7	42.09(75.76)
15	28.1 ± 0.6	37.2 ± 1.2	45.4 ± 1.8		31.8 ± 1.9	41.1 ± 1.0	66.4 ± 2.4	
20	34.9 ± 1.5	44.3 ± 2.1	63.7 ± 2.0		39.7 ± 0.4	59.8 ± 1.5	74.1 ± 0.7	
25	38.1 ± 1.2	47.3 ± 1.7	68.2 ± 1.5		43.1 ± 1.1	61.7 ± 1.7	81.8 ± 0.6	
30	42.8 ± 1.0	55.4 ± 1.1	75.5 ± 1.3		49.7 ± 0.8	67.4 ± 1.1	89.7 ± 1.4	

compound **2**, plus the presence of an OH phenolic group and another benzene ring in the structure. As a result, the activity of compound **3** is greater than that of compound **2** when used alone or in combination with a polyurethane varnish. The pyridine derivatives exhibit antifungal activity against *A. niger* and *Alternaria alternata* according to a prior research, and this is owing to the antifungal activity of various groups contained in the produced pyridine derivatives.[7,49] Anti-fungal characteristics, doubling the paint's lifespan and preventing the spread of fungal infection in public areas and health care facilities. According to Murugesan and colleagues, the pyridine molecule displays a potent inhibitory effect against *A. flavus*, *Penicillium sp*., and *A. niger*, as well as considered activity against *A. fumigatus*.[50] The order activity for the obtained results can represented as derivative **2** with polyurethane > derivative **3** with polyurethane > Blank formulation (pure PU varnish).

Adulticidal assay of the prepared pyridine derivatives

The insecticidal activity of the title compounds was tested against house fly *Musca domestica* and the bioassay results are given in Tables 4 and 5. The results of the initial screening showed that 10 ppm of the newly synthesized compounds have moderate to moderate activities. The mortality rates of comp. **2** and **3** against house fly recorded at 50.7 and 68.0%, while with increasing concentrations lead to an increase the mortality percentage, were high morality reported with concentrations 30 ppm presented 89.5 and 91.5% for comp. **2** and **3**, respectively. The concentrations 15, 20 and 25 ppm exhibited high activities against house fly, with mortality rates of 60.1%, 71.3%, and 63.7%, respectively, for comp. **2**. While with comp. **3** at the same concentrations give 72.4, 80.6, and 83.8%, respectively. As shown in Table 4. Data in Table 5 recorded those two compounds mixed with PU varnish showed variable mortality (40.1 – 87.7%) at the concentrations 10.0, 15, 25, and 30 ppm after 72 h of treatment were given 40.1, 45.4, 63.7, 68.2, and 75.5% adulticidal mortality, respectively, with compound **2**, while with compound **3** at the same concentrations give 58.3, 66.4, 74.1, 81.8, and 89.7% adulticidal mortality, respectively. The lethal concentration (LC_{50} (LC_{90})) for two compounds (**2** and **3**) was recorded at 33.04(59.47) and 51.85(91.33) against the adulticidal activity of house fly, while LC_{50} (LC_{90}) for two compounds (**2** and **3**) complex with paint recorded 28.06 (50.51) and 42.09 (75.76) %, respectively, against house fly *Musca domestica*. Many insects are pests and can be serious threats to buildings. Insecticides represent an elective way to control pest insects but are harmful to the environment. Many insects are considered pests because they pose a serious threat to agriculture, forestry, buildings, and human health.[51,52] Chemical treatments are widely used to tackle insect pests and included insecticide sprays, groom able coatings, baits, soil termiticide injection and chemical fumigation.[53] Laboratory assays pyridine comp. against house fly *M. domestica* point at the PU varnish's potential in attaining high mortality rates for up to 12 months despite resistance status. Ways to deal with the porosity of certain materials need to be explored. Pyridine's effect on the mortality of exposed adult house fly affords an added tool in reducing overall pest and pathogen vector population densities when the lethal effect of OPs reduces over time. The PU coating is readily applied and improves communities' homes. In this work, we focused on developing new insecticide agents based on their biological activity and incorporating them into PU varnishes formulations then evaluating their physical and mechanical properties, as well as their insecticide activity. Future goals include performing a large-scale entomological, epidemiological, and community acceptability study in Africa.[13] The activity of chemical compounds against mosquito is represented in terms of their medium lethal concentrations LC_{50} (LC_{90}), which recorded 0.90(1.62), 0.89(1.61), and 0.86(1.56) g/mL for **3** and **2** chemical compounds, respectively, after 72 h from treatment. On the other hand, the house fly treatments by the three compounds showed approximately the same

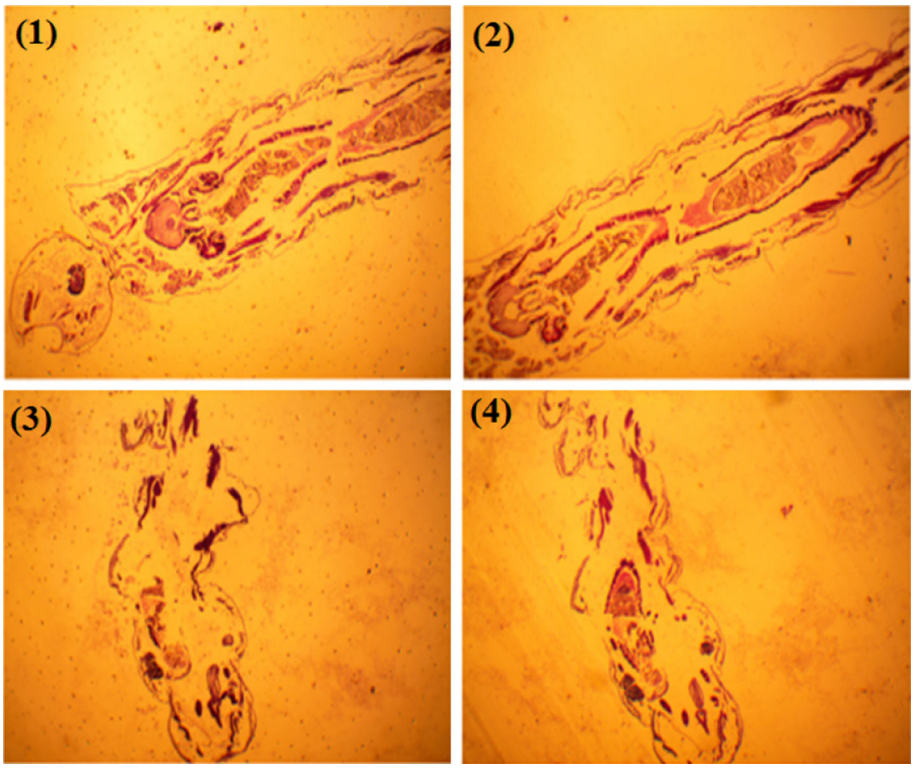


Fig. 5: Histological scan of the alimentary canal of house fly *Musca domestica*. (1 and 2) control, (3) treatment with 2 pyridine derivatives (comp. 2), and (4) treatment with pyridine derivatives (comp. 3) (Color figure online)

effect with LC_{50} (LC_{90}) values of 0.88(1.59), 0.85(1.54), and 0.90(1.63) g/mL, for 3 and 2 chemical compounds, respectively. The histological scan of the alimentary canal of house fly *M. domestica*. (1 and 2) control, (3) treatment with **2** pyridine derivatives (comp. **2**), and (4) treatment with pyridine derivatives (comp. **3**) was represented as in Fig. 5.

We believe that antimicrobial activity results contribute to circumventing the accumulation of organisms and insects on the coating surfaces and contribute to the hazardous materials and ecological coating chemistry.

Conclusions

Pyridine derivatives are prepared and evaluated before being incorporated into polyurethane coating formulations to create antifungal and insecticidal coating compositions. The prepared organic compounds were confirmed by FTIR, mass, ^{1}HNMR, and ^{13}C NMR spectra. Polyurethane varnish was embedded with the prepared compounds **2** and **3**. Polyurethane coatings were applied to substrates to measure coating properties. Coating features explored include gloss, scratch resistance, flexibility, and adhesion; mechanical properties include impact resistance and Shore hardness; and physicochemical properties include chemical resistance of coated polyurethane samples. The results of the experiments revealed that all polyurethane coatings based on dihydropyridine derivatives had good performance and durability based on the observed results of gloss which varied from 65 to 85, and scratch resistance which varied from > 1.5 to > 2 kg, and adhesion were confirmed that, in addition to excellent chemical resistance, as evidenced by their physicochemical properties. The observed antifungal and insecticide activities indicated that dry wood coated with polyurethane based on dihydropyridine derivatives is promising for resistance to these insects and fungi. In comparison with the paint as blank, the results revealed that the inhibition zones diameter by compound **2** were 25.1 ± 0.69, 23.2 ± 0.94, 20.16 ± 0.62, 20 ± 0.80, and 18 ± 0.81 mm against *A. terreus, A. niger, A. flavus*, *and C. albicans*, *A. fumigatus*, respectively, whereas the inhibition zones (IZ) diameter by compound **3** were 22.56 ± 0.30, 21.03 ± 0.49, 21.03 ± 0.61, 21 ± 0.66, and 20 ± 0.78 mm versus *A. niger, A. fumigatus A. flavus*, *C. albicans*, and *A. terreus*, respectively. The biological activity and insecticide activity of the prepared organic compound before and after incorporation with polyurethane, and the dose concentration of the pyridine derivatives were investigated.

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