

SYNTHESIS OF SOME ANTIOXIDANT AND
ANTICORROSIVE ADDITIVES FOR
GASOLINE MOTOR OILS

H. M. Hassan; O. M. O. Habib; M. Y. El-Saidy
and A. M. A. El-Hoseny

*Chemistry Dept., Faculty of Science, Mansoura University,
Mansoura, Egypt. e. mail: Hassantemtem@yahoo.com*

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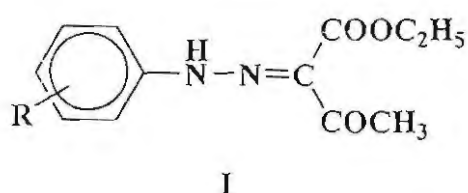
ABSTRACT

In the internal combustion engines, lube oils suffer from autoxidation as a result of contact with oxygen (air) at elevated temperature for long periods and in contact with metals, i.e. iron, copper, lead, etc, used in the manufacture of the engine. These metals act as catalysts for oxidation, thus resulting in the formation of oxygenated oil soluble and insoluble compounds which exert adverse effect on the performance of lube oil by causing among other effect, increasing their viscosity, corrosion of the metal parts and a general dirtiness of the system with sludge and varnishes. For these reasons, different types of antioxidant additives are usually added to the oil in order to control oil oxidation.

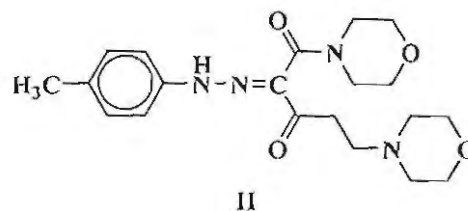
RESULTS AND DISCUSSION

The present investigation is a continuation to our previous studies on the synthesis of lube oil additives [Hassan et al., (1985); Hassan et al., (1988); Hassan et al., (2000) and Hassan (1998)]. It concerns with the synthesis of some heterocyclic organic compounds that are belonging to pyrazole, pyridazine, triazine, benzothiazole and thienopyridazine derivatives and evaluation their efficiency as oxidation and corrosion inhibitors for some local gasoline motor oils.

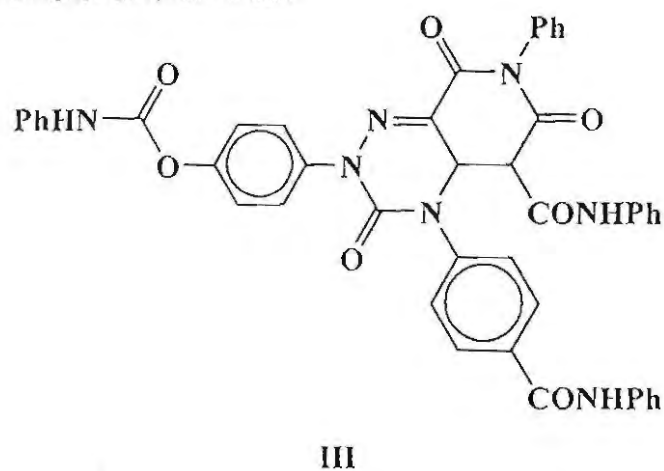
Thus, 1,5-dimorpholine-4-yl-2-(p-tolylhydrazono)pentan-1,3-dione **II** was prepared by refluxing ethyl p-methylphenylhydrazono acetoacetate **Ia** with morpholine hydrochloride and paraformaldehyde in ethanol as a solvent.



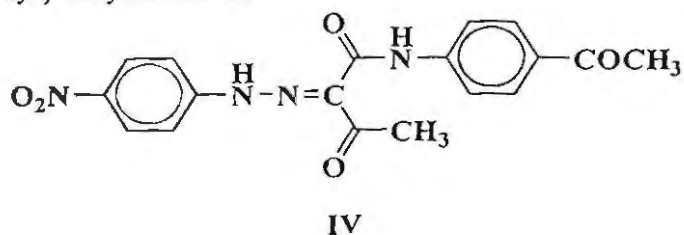
- I a; R = p-CH₃
 b; R = p-NO₂
 c; R = p-OH
 d; R = m-NO₂

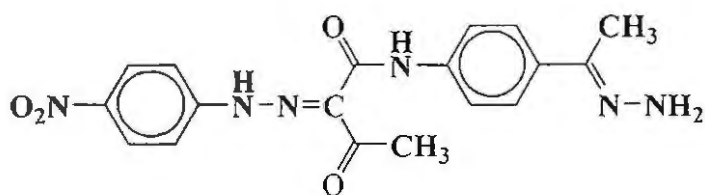


The azodye **Ic** was reacted with phenyl isocyanate in pyridine to give pyridotriazine derivative **III**.



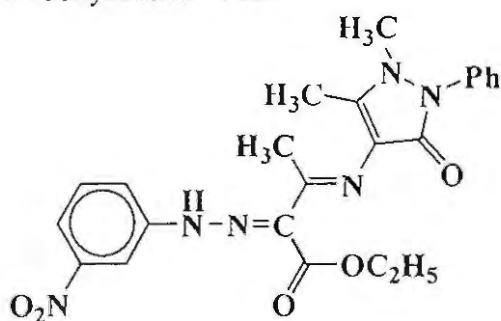
On the other hand, reaction of azodye **Ib** with p-aminoacetophenone in sodium ethoxide afforded 2-(4-nitrophenylhydrazono)-3-oxo-N-(4-acetylphenyl) butyramide **IV** [Hassan et al., (2000)], which on treatment with hydrazine hydrate in ethanol gave 2-(4-nitrophenylhydrazono)-3-oxo-N-{4-[1-(hydrazono)-ethyl]-phenyl} butyramide **V**.





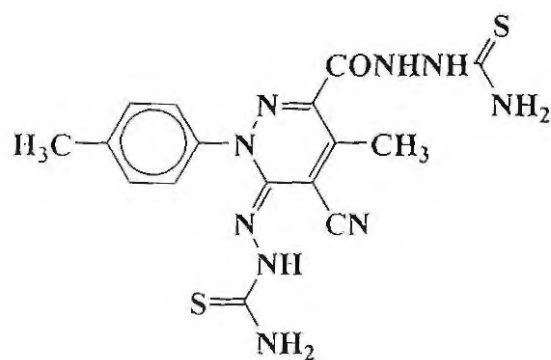
V

Reaction of azodye **Id** with 4-aminoantipyrine in xylene gave 3-(4-antipyrinylimino)-2-(3-nitrophenylhydrazono)butyric acid ethyl ester **VI**. On the other hand, ethyl 1,6-dihydro-1-(p-tolyl)-5-cyano-4-methyl-6-oxopyridazine-3-carboxylate **VII** was reacted with hydrazine hydrate in ethanol to give 1,6-dihydro-1-(p-tolyl)-5-cyano-4-methyl-6-oxopyridazine-3-carbohydrazide **VIII**.

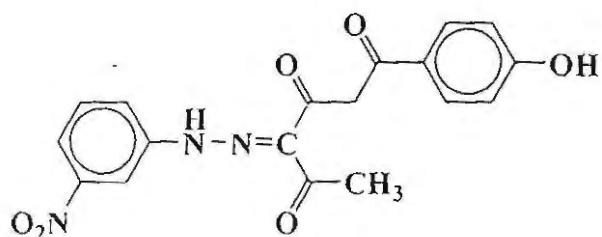


VI

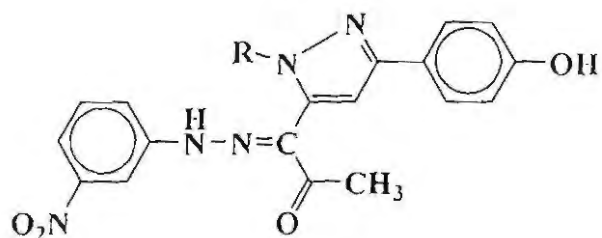
Also, pyridazine carboxylate **VII** was reacted with thiosemicarbazide in glacial acetic acid to give 3-(N-thiocarbamoyl carbohydrazide)-5-cyano-4-methyl-1-(p-tolyl)-6-thiosemicarbazone pyridazine **IX**. On the other hand, reaction of azodye **Id** with p-hydroxyacetophenone in sodium ethoxide afforded [(1-p-hydroxybenzoyl)-3-(3-nitrophenylhydrozono)]pentan-2,4-dione **X** [Hassan et al., (2000)], which on reaction with hydrazine hydrate in ethanol and with phenylhydrazine HCl in acetic acid gave 1-[5-(4-hydroxyphenyl)-4H-(pyrazol-3-yl)]-1-[(3-nitrophenyl)-hydrazono]propan-2-one **XIa** and 1-[5-(4-hydroxyphenyl)-4H-(2-phenylpyrazol-3-yl)]-1-[(3-nitrophenyl)-hydrazono]propan-2-one **XIb**, respectively.



IX

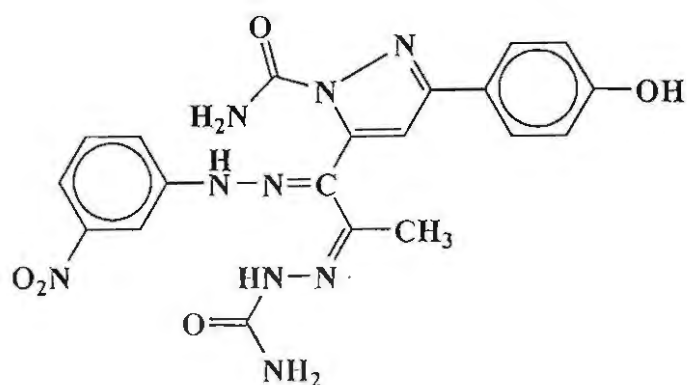


X

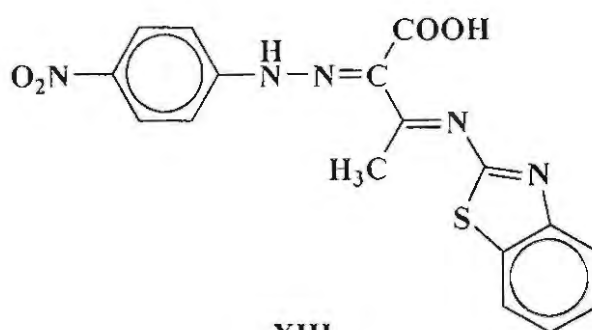

 XIa; R = H
 b; R = Ph

On the other hand, treatment of **X** with semicarbazide hydrochloride in glacial acetic acid gave 1-[5-(4-hydroxyphenyl)-4H-2-carbamoylpyrazol-3-yl]-1-(3-nitrophenylhydrazono)-2-semicarbazone propan-2-one **XII**.

Reaction of azo dye **Ib** with 2-aminobenzothiazole in ethanol gave 3-(2-benzothiazolylimino)-butyric acid-2-(p-nitrophenylhydrazono) **XIII**.

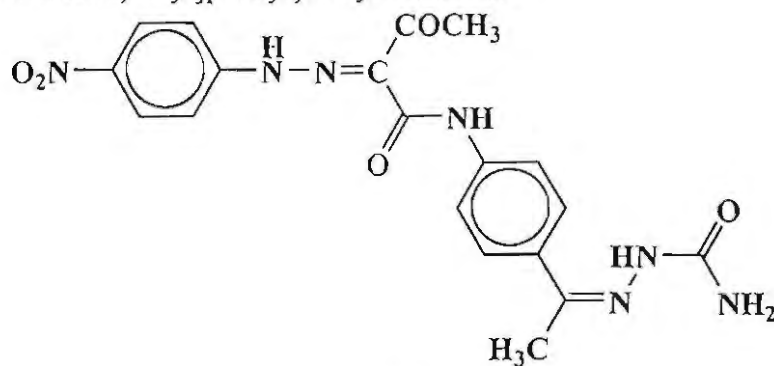


XII



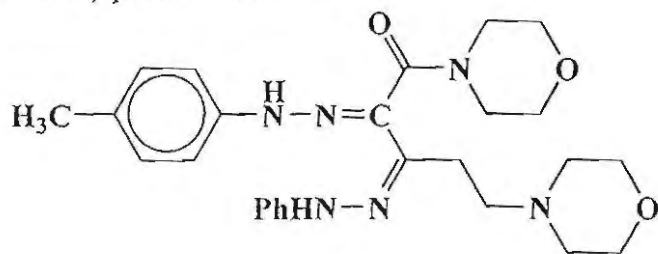
XIII

On the same way, compound IV was reacted with semicarbazide hydrochloride and gave 2-(4-nitrophenylhydrazono)-3-oxo-N-{4-[1-(semicarbazono)ethyl]phenyl} butyramide XIV.



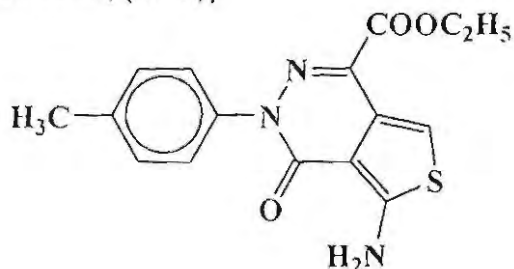
XIV

By treating compound II with phenylhydrazine hydrochloride in glacial acetic acid, it gave 1,5-dimorpholin-4-yl-3-(phenylhydrazono)-2-(p-tolyldiazono)-pentan-1-one XV.



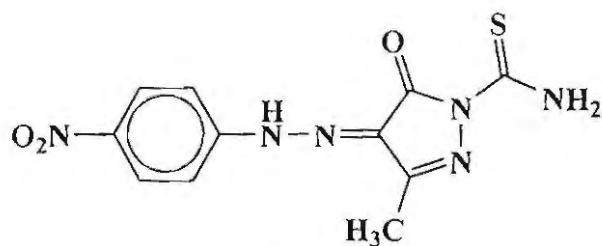
XV

On the other hand, reaction of pyridazine VII with sulfur in ethanol afforded 5-amino-3,4-dihydro-3-(4-tolyl)-4-oxo-ethyl thieno[3,4-d]pyridazine-1-carboxylic acid XVI [Zeman et al., (1987); Zeman et al., (1985) and Hu et al., (1999)].

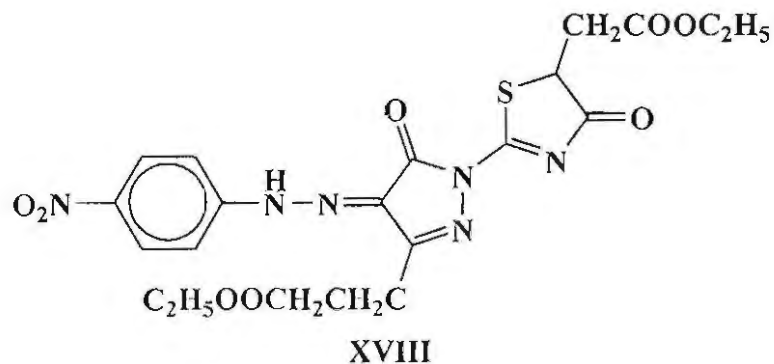


XVI

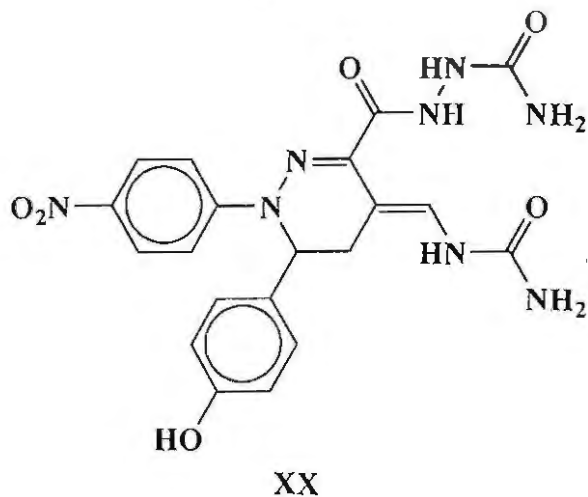
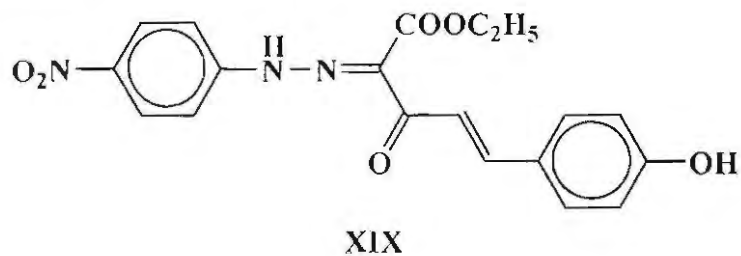
Treating of 4-(p-nitrophenylhydrazono)-N¹-thiocarbamoyl-3-methyl-2-pyrazolin-5-one XVII [Hassan (1998)] with ethyl chloroacetate gave 3-{1-(5-ethoxycarbonyl)-methyl-4-oxo-4,5-dihydrothiazol-2-yl)-4-[4-nitrophenyl hydrazono]}-5-oxo-4,5-dihydro-1H-pyrazol-3-yl}-ethyl propanoate XVIII.



XVII



Also, treating of ethyl 2-(p-nitrophenylhydrazono)-5-(p-hydroxyphenyl)pent-4-ene-3-oneate **XIX** with semicarbazide hydrochloride gave 1,4,5,6-tetrahydro-3-carboxylic acid semicarbazide-6-(4-hydroxyphenyl)-1-(p-nitrophenyl)pyridazine-4-semicarbazone **XX** [Abou ElNaga & Salem (1984); Sommer (1988); Okada & Yamashita (1986) and Papke et al., (1989)].



The structure of the last compounds were elucidated by ir spectra, nmr spectra, chemical analysis by Asmaa Moshali Abd-Alah El-Housiny, M. Sc., Mansoura University, Faculty of science, Chemistry Department (2003) as shown in table (1) [El-Housiny (2003)].

Table (1) : Characterization of the prepared organic compounds.

Comp. No.	m.p. (°C) solvent of cryst.	Colour	Yield %	Mol. Formula	Chemical analysis Calc. (Found)		
					C%	H%	N%
II	192-5 Ethyl alc.	Yellow	68	C ₂₀ H ₂₈ N ₄ O ₄	61.86 (61.70)	7.27 (7.22)	14.4 (14.11)
III	244-6 Acetic acid	White	90	C ₄₅ H ₃₁ N ₇ O ₇	71.7 (71.8)	4.07 (4.2)	13.3 (13.3)
V	169-172 Acetic acid	Orange	85	C ₁₈ H ₁₈ N ₆ O ₄	56.5 (56.9)	4.7 (4.5)	21.9 (21.8)
VI	190 Xylene	Reddish brown	87	C ₂₃ H ₂₄ N ₆ O ₅	59.4 (59.1)	5.1 (4.9)	18.1 (17.9)
VIII	204-6 Benzene	Brown	60	C ₁₄ H ₁₃ N ₅ O ₂	59.3 (59.3)	4.6 (4.8)	24.3 (24.5)
IX	267 Xylene	Yellow	71	C ₁₆ H ₁₇ N ₉ OS ₂	47.08 (47.1)	4.2 (4.3)	27.92 (28.0)
XIa	262-4 Acetic acid	Yellow	67	C ₁₈ H ₁₅ N ₅ O ₄	59.2 (59.2)	4.1 (3.9)	19.2 (19.5)
XIb	169-70 Ethyl alc.	Orange red	70	C ₂₄ H ₁₉ N ₅ O ₄	65.3 (65.2)	4.3 (4.3)	15.87 (15.9)
XII	260-2 Ethyl alc.	Yellow	75	C ₂₀ H ₁₉ N ₉ O ₅	51.6 (51.3)	4.1 (4.1)	27.1 (27.3)
XIII	240-3 Ethyl alc.	Green	68	C ₁₇ H ₁₃ N ₅ O ₄ S	53.26 (53.08)	3.9 (4.0)	18.3 (18.2)
XIV	266 Acetic acid	Yellow	74	C ₁₉ H ₁₉ N ₇ O ₅	53.6 (53.3)	4.4 (4.3)	23.05 (23.05)
XV	128-9 Xylene	Orange yellow	70	C ₂₆ H ₃₄ N ₆ O ₃	63.78 (64.29)	7.0 (6.9)	16.3 (16.42)
XVI	199-200 Ethyl alc.	Yellow	75	C ₁₆ H ₁₅ N ₃ O ₃ S	58.3 (58.6)	4.5 (4.8)	12.7 (12.4)
XVIII	264-8 Ethyl alc.	Brownish yellow	66	C ₂₁ H ₂₂ N ₆ O ₈ S	48.65 (49.00)	4.2 (4.2)	
XX	279-80 Acetic acid	Greenish yellow	65	C ₁₉ H ₁₉ N ₉ O ₆	48.7 (48.8)	3.8 (3.9)	26.9 (26.7)

1- Evaluation of the prepared compounds as antioxidant additives for lube oil

To verify the effect of the prepared compounds as antioxidant, 0.1g was added to one litre of the used lube oil free from any additives were subjected to severe oxidation at 155 °C with air at a rate of 10 litre/hour for 36 hours. Samples were taken at regular intervals of six hours and tested for their oxidation stability expressed in terms of the total acid number (T.A.N.) according to ASTM D-3242 and U.V. spectra.

It is obvious from the obtained results that in the absence of additives, the oxidation products increased with time. When the prepared additives **II-XX** were added to the used oil at concentration 0.1 g/litre the oxidation products increased also with time but at a rate much less than those without additives. Thus, table 2 and figures 1-5 reveal that the total acid number (T.A.N.) of the oil samples containing the prepared compound after 36 hours oxidation showed good oxidation resistance properties to the used lube oil compared with the undoped oil and that compounds **II, III, IX, XIa, XIII, XVIII** and **XX** exhibit the highest antioxidant activity. Compound **II** was effective as antioxidant (acid number 0.68 mg KOH/g oil) due to the presence of some antioxidant groups as morpholine, carbonyl and amino groups but compound **III** was the most effective antioxidant compound due to the presence of three amidic groups and pyridotriazine heterocyclic rings. Also, additive **IX** was a good antioxidant due to the presence of amino, thioamide, imino groups and pyridazine heterocyclic ring. Compound **XIa** was also good antioxidant groups as amidic, carbonyl, imino groups and pyridotriazine heterocyclic ring but the additive **IX** was also a good antioxidant (acid value = 1.66 mg KOH/g oil) after 36 hours of oxidation due to presence of amino, thioamide, imino groups and pyridazine heterocyclic ring. Compound **XIa** was a very good antioxidant (acid number = 1.11 mg KOH/g oil) due to presence of amino, imino, ketonic, phenolic groups and pyrazole ring. Also, compound **XIII** had a good antioxidant effect (acid value = 1.24 mg KOH/g oil) due to presence of amino, imino and benzothiazole ring. Also, compound **XVIII** has a good antioxidant (acid value = 1.38 mg KOH/g oil) after 36 hours of oxidation due to the presence of amino, imino groups, pyrazole and thiazole heterocyclic rings and compound **XX** has also good antioxidant effect (acid number = 1.63 mg KOH/g oil) after 36 hours of oxidation due to the presence of different groups like imino, semicarbazone, phenolic groups and pyridazine heterocyclic ring.

Table (2) : Variation of the T. A. N. with oxidation time of the used lube oil samples without and with selective additives II-XX containing 0.1 g/litre concentration at 155 °C up to 36 hours.

Compound no.	Time (hour)						T. A. N. (mg KOH per gram sample)
	6	12	18	24	30	36	
Oil without additive	0.92	1.32	1.92	2.46	2.84	3.24	
II	0.146	0.15	0.23	0.31	0.41	0.68	
III	0.112	0.112	0.16	0.2	0.24	0.28	
V	0.52	0.72	0.96	1.08	1.52	1.88	
VI	0.8	1.2	1.78	2	2.27	2.28	
VIII	0.68	1.04	1.76	2.32	2.6	3.06	
IX	0.57	0.92	1.08	1.27	1.5	1.66	
XIa	0.22	0.28	0.42	0.56	0.8	1.11	
XIb	0.3	0.54	0.76	1.08	1.4	1.63	
XII	0.6	0.88	1.16	1.4	1.72	1.84	
XII	0.19	0.46	0.9	1.1	1.2	1.24	
XIV	0.46	0.8	1.12	1.4	1.69	1.8	
XV	0.52	0.84	1.24	1.6	1.86	2.04	
XVI	0.34	0.72	1.1	1.36	1.58	1.84	
XVIII	0.6	0.88	1.08	1.27	1.3	1.38	
XX	0.3	0.54	0.68	0.8	1.4	1.63	

2. Evaluation of the prepared compounds as corrosion inhibitors for the used lube oil

In the present work, the prepared compounds which showed antioxidant efficiency were tested as corrosion inhibitors for the corresponding lube oil using four different strips of copper, iron aluminum and nickel with an area of 1 cm². The results reveal that there are decrease in corrosion products when using the oil containing these additives in comparison with oil free from additives. It was also found that all compounds II – XX show higher corrosion inhibition than oil without additives and this could be due to the presence of anticorrosive moieties. On the other hand, it was found that compounds II, III, VIII, IX, XIa, XII and XIII were the best corrosion inhibitor for all the used metals (table 3) which could be explained due to the presence of heterocyclic moieties as triazine, pyridazine and pyrazoles in their structures. These results agree with that reported by Gad Allah et al.

3. Effect of concentration

It was interesting to study the effect of concentration of additives that gave the highest antioxidant efficiency for the used lubricating oil in

order to find the optimum concentration recommended to be used. Thus, three different concentrations of additives **II** and **III** namely, 0.1; 0.05 and 0.1 g/liter were used. The total acid numbers of oil were determined as shown in table 4. The obtained results illustrated that increasing the additive concentration leads to decrease of oxidative products as indicated by decrease in the total acid numbers. It was also indicated that the concentration 0.1 g/liter of the additive is the more effective concentration to be used.

Table (3) : Effect of additive types containing 0.1 g/liter concentration on the weight loss of metals (iron, copper, aluminum and nickel) after 36 hours oxidation at 155°C with air rate 10 liter/hour.

Compound no.	Weight loss (10g)			
	Fe	Cu	Al	Ni
Oil without additive	15	22	13	12
II	0.3	3	2	0.1
III	0.3	3.4	0.4	0.2
V	3	9	1	0.1
VI	3.4	4	2	0.1
VIII	0.2	2.1	0.3	0.2
IX	5.3	6.3	1.1	0.4
XIa	0.1	3	0.4	0.1
XIb	0.5	3.5	1.4	0.1
XII	0.1	4.2	0.3	0.4
XIII	1	4.3	1.2	1
XIV	6	10	7	5
XV	2	5	4	0
XVI	3	3.7	1.8	1
XVIII	4	5	1.3	1.1
XX	3	5	1	0.1

Table (4) : Variation of the acid value with oxidation time of the used lube oil samples without and with different concentrations of additives II and III at 155 °C up to 36 hours.

Compound no.	Concentration g/liter	Time (hour)						T. A. N. (mg KOH per gram sample)
		6	12	18	24	30	36	
Without additives	-	0.92	1.32	1.92	2.46	2.84	3.24	
Additive II	0.01	0.54	0.81	0.84	1	1.3	1.4	
	0.05	0.21	0.4	0.5	0.6	0.9	1.13	
	0.1	0.146	0.15	0.23	0.31	0.41	0.68	
Additive III	0.01	0.8	1.16	1.36	1.44	1.44	1.44	
	0.05	0.6	0.96	1.04	1.04	1.09	1.18	
	0.1	0.11	0.11	0.16	0.2	0.24	0.28	

4- Thermal stability of prepared antioxidant additives

Some of the highly effective antioxidant additives, namely, **II**, **III**, **IX**, **XIa** and **XIII** were subjected to thermal analysis using TGA and DTGA techniques. The results are illustrated in table 5. The data indicated that, the first stage of decomposition for compound **II** began at 151.69 °C and for product **III** at 210.26 °C, respectively and end at 216.04 and 265.6 °C with weight loss 99.55% and 99.44 %, respectively.

Also, compounds **IX**, **IXa** and **XIII** began in their decomposition in first stage at 236.64, 214.43 and 227.92 °C and their decomposition end at 304.72, 279.2 and 304.97 °C, respectively.

Table (5) : Thermal analysis for different additives.

Compound no.	Start (TGA) °C	End (TGA) °C	Weight loss (%)
II	151.69	216.04	99.55
III	210.26	265.64	99.44
V	190.34	254.29	21.35
VI	178.5	218.14	2.17
VIII	226.43	310.83	28.43
IX	236.64	304.72	89.25
XIa	214.43	279.20	99.56
XIb	216.26	324.97	73.60
XII	212.07	295.28	96.99
XIII	227.92	304.97	92.19
XV	201.35	297.61	55.15
XVI	217.39	306.50	72.45
XVIII	218.05	295.80	51.44
XX	200.35	305.32	99.33

5- A comparison between the oxidation stability of the used oil containing the prepared products with a lube oil containing a commercial additive.

It was also interest to compare the oxidation stability of the used lube oil containing the highly efficient prepared antioxidants (0.1 g/litre) with a lube oil containing a commercial antioxidant additive purchased from the local market (CO-OP Cosf/ cc 21 w/51 oil). The results obtained after 36 hour oxidation at 155 °C with air rate 10 litre/hour as shown from table 6 which illustrated that the lube oil containing the compounds II and III show oxidation stability comparable to the other and in some cases are better than that of the used commercial lube oil.

Table (6) : Evaluation of the used lube oil additives comparison with commercial lube oil sample.

Compound no.	Time (hour)						T. A. N. (mg KOH per gram sample)
	6	12	18	24	30	36	
Without additives	0.92	1.32	1.92	2.46	2.84	3.24	
Commercial oil	0.42	1.01	1.23	1.23	1.57	1.57	
Additive II	0.146	0.15	0.23	0.31	0.41	0.68	
Additive III	0.11	0.11	0.16	0.20	0.24	0.28	

1- Evaluation of the prepared compounds as antioxidant additives for the used lube oil

A lube oil sample free from additives as well as different blends of the oil containing different concentration of the prepared products have been subjected to severe oxidation with an air rate of 10 litre/hour at 155 °C for 36 hours.

Samples were taken at regular intervals of six up to 36 hours of oxidation. The oxidation stability of these samples expressed in term of the total acid number (T. A. N.) which has been evaluated according to ASTM D-3242. The results are gives in table 2.

2- Evaluation of the prepared compounds as corrosion inhibitor additives fro the used lube oil

In order to evaluate the corrosion inhibition of the used lube oil samples containing the prepared compound, strips of four metals; iron, copper, aluminum and nickel, were used in this study. Every metal was

purified from its oxide, weighted and then immersed in the oxidation system for 36 hours under the previous conditions. Then it was purified and its weight has been again determined. The difference in weight was calculated and the efficiency of the used products as corrosion inhibitor was evaluated by using the weight loss technique according to ASTM D-130 as shown in table 3.

3- Effect of concentration

It was interesting to study the effect of concentration of additives that gave highest antioxidant efficiency for the used lubricating oil in order to find the optimum concentration recommended to be used. Thus, three different concentration of additives II and III namely, 0.01; 0.05 and 0.1 g/litre were used. The total acid numbers of oil were determined as shown in table 4.

4- Evaluation of the oil samples after oxidation by ultraviolet radiation

Ultraviolet spectra were carried out to lubricating oil after 36 hour of oxidation using all additive (II-XX) and oil without additives using air rate 10 litre/hour at 155 °C. The oil samples were diluted to 104 times with diethyl ether then exposed to ultraviolet radiation by Unicam UV2/Visible spectrometer equipment.

5- Surface tension of oil after oxidation

Surface tension was carried out to the oil with and without additives after 36 hours at 155 °C with air rate 10 litre/hour in order to determine the detergency effect of additives on oil by using surface tension apparatus (Torrison Balance White Elec. Insy. Co, LTD. No 0/17604f).

6- Thermal stability of prepared antioxidant additives

In order to study the stability of the effective antioxidant and anticorrosive additives towards heat, thermal analyses using TGA and DTGA technique were studied by using Shimadza TGA apparatus. The results are shown in table 5.

7- A Comparison between the oxidation stability of the used oil containing the prepared products with lube oil containing commercial additive

It was also interest to compare the oxidation stability of the used lube oil containing the highly efficient prepared antioxidants (0.1 g/litre)

with a lube oil containing a commercial antioxidant additive purchased from the local market (CO-OP Cosf/ cc 21w/51 oil). The results obtained after 36 hours oxidation at 155 °C with air rate 10 litre/hour are shown in table 6 and figure 20

Note: all these additives has no effect on detergency index, viscosity, foam tendency, APS gravity, and aniline point of the used local gasoline motor oil.

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تحضير بعض المركبات غير متجانسة الحلقة بإضافات موانع للأكسدة
والتآكل لزيوت تشحيم موتورات الجازولين

تم تحضير عدد ٢٠ مركبا غير متجانس الحلقة و تم اثبات التركيب الكيميائى لهذه المركبات كما تم استخدامها كإضافات للجازولين كموانع للأكسدة و التآكل. حيث أظهرت هذه المركبات قدرة فائقة فى منع عملية الأكسدة و التآكل لبعض المعادن مثل الحديد و الألمونيوم و النحاس. كما أن هذه المركبات قد قورنت بما يتم استخدامه فى السوق من إضافات حيث أظهرت تفوقا على هذه المركبات التى يتم استخدامها فى السوق و هذه المركبات سهلة التحضير و رخيصة الثمن و الكميات المستخدمة منها قليلة جدا و غير مؤثرة على البيئة ولا على الإضافات الأخرى التى يتم استخدامها لزيوت التشحيم. كما ان ليس لها تأثير واضح على الخواص الفيزيائية لزيوت التشحيم