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# The Effect of Operating Conditions of Urea Dewaxing on the Pour Point of Light Lubricating Oil.

**Abdul-Halim A.Mohammed* and Noor S.Akram**

**Chemical Engineering Department - College of Engineering - University of Baghdad – Iraq*

## Abstract

*An investigation was conducted for dewaxing of lubricating oil fraction by urea to reduce the pour point.In this study mixture of 45 % methyl ethyl ketone (MEK) and 55 % toluene was used as a solvent. The studied variables are mixing time (10-70 min), solvent to oil volume ratio (0.5:1- 2:1), urea to wax weight ratio (2- 6) and constant mixing speed 1500 rpm. By analysis of the experimental results, the best operating conditions achieved are mixing time 40 min, solvent/oil 2:1 volume ratio, and urea/wax 4:1 weight ratio. At these conditions the pour point of the lubricating oil decreases from 24 ° C to -13 °C.*

***Keywords*****:** urea dewaxing, adduct, solvents, pour point.

## Introduction

Wax is probably the most troublesome product in the manufacture of lubricating oil. Its presence in lubricating oils prevents free movement at lower temperatures [1]. So all lube stocks must be dewaxed, except those from a relatively few highly naphthenic crude oils or those which do not flow properly at ambient temperatures [2].

Many methods were used to remove the wax from lubricating oil distillate. The first process is solvent dewaxing process; solvent dewaxing can be applied to light, intermediate, and heavy lubricating oil distillates [3]. The main process steps include mixing the feedstock with the solvent, chilling the mixture to crystallize wax, and recovering the solvent [4].

The second process is catalyst process. Catalytic dewaxing is a hydrocracking process and is therefore operated at elevated temperatures (280 to 400 °C) and pressures (300 to 1500 psi) [3], it removed n-paraffins and waxy side chains from other molecules by catalytically cracking them into smaller molecules [5].

The third process is called urea dewaxing. Urea dewaxing is a process for producing low pour point oils, and using urea which forms a solid complex (adduct) with the straight chain wax paraffins in the stock. In contrast to the other dewaxing techniques, urea dewaxing can be achieved without the use of refrigeration, the process may be particularly useful for production of refrigerator oils, transformer oils, and the like [3].

In addition, the purity of recovered n-paraffin is often very low because of non-normal hydrocarbons participating in the adduct formation [6].

Because of the oil viscosity, good contact between oil and urea is not achieved and difficulties are encountered during filtration, it is necessary to use a solvent to avoid these troubles. This solvent must dissolve oil and wax but not the urea [7]. It is also known that the selectivity of the urea dewaxing process may be improved by diluting the mineral oil distillate with oil solvents. Suitable oil solvents include low molecular weight alcohols and ketones, low boiling hydrocarbon such as butane, pentane, isopentane, hexane, and the like, and halogenated hydrocarbons such as dicloromethane can be used [8].

Urea selectively crystallizes around paraffinic hydrocarbons with long straight chains to make a solid, filterable complex or adduct. This selectivity of adduct formation is a function of the cross section of the hydrocarbon molecules as related to the geometry of the urea crystal, Figure 1 shows these relationships for different hydrocarbon molecules [9].

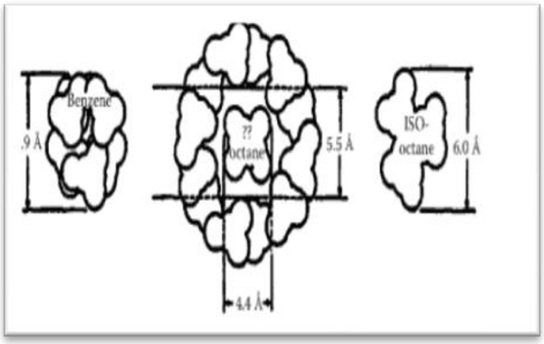

Figure 1 Relative sizes of urea adduct and specific hydrocarbons (9)

The condition in the reactor (temperature, water content, urea to feed and solvent to feed ratio, flow and mixing, type of solvent and/or activator, etc.) will determine the structure of the adduct [10].

X-ray studies indicate that the crystal structure of urea changes from a tetragonal to a hexagonal system during the complex formation process. The urea molecules wrap around the straight chain molecules in a hexagonal spiral; the spirals form channels having a diameter of approximately 5 ˚A, large enough to accommodate straight chain molecules but not branched chain or cyclic molecules [6].

Several previous studies have investigated the reduction of pour point by urea dewaxing. Yata[11] used residual oil as feed to remove wax by using urea with the methanol-benzene solvent mixture. It was indicated that the pour point of each distillate fraction does not differ much with the solvent-dewaxed oil, but increases as the fraction becomes heavier with the urea-dewaxed oil. Mead and Wright[12] improved urea dewaxing process for naphthenic distillate using urea/alcohol slurry chilled to 60 to 65 °F for production of refrigerator oil with improved low temperature properties. Yasin[13] made an investigation for the process of urea pour point reduction of heavy lubricating oil fraction Methyl iso-butyl ketone and methylene chloride solvent were used. It was found that the pour point of the feed stock was lowered from 34 °C to about 4 °C when methyl iso-butyl ketone solvent was used while the pour point of the fraction lower to 7 °F when methylene chloride was used.

This work deals with the study of the effect of operating condition on the urea dewaxing process of light lubricating oil fraction.

## Experimental Work

### Materials

A raffinate of furfural extraction of light lubricating oil fraction produced by vacuum distillation in Al-Duara Refinery was used in this investigation as feed stock. Table 1 shows the properties of the lubricating oil fraction.

Table 1 Properties of light lubricating oil fraction.

| ***No.*** | ***Specification*** | ***value*** |
|---|---|---|
| 1 | Specific Gravity @ 60/60 $^{o}$F | 0.860 |
| 2 | Viscosity, Cst, @ 40 $^{o}$C | 24 |
| 3 | Viscosity, Cst, @ 100 $^{o}$C | 4.6 |
| 4 | Viscosity Index | 115 |
| 5 | Pour Point, $^{o}$C | 24 |
| 6 | Color | 1.0 |

Mixture of 45% of MEK and 55% of toluene was used as a solvent. The MEK causes the wax in the oil to crystallize, and the toluene is used to dissolve the oil. Both the wax solution and the oil solution are distilled for removal of solvent (to be reused) and to provide solvent free wax and oil. Thus the two products are wax-free oil and an oil-free wax .

Urea (carbamide or carbonyl diamide) is a colorless crystalline compound, formula $CH_4N_2O$ with a nitrogen content of 46%. Urea is a highly soluble in water. It is supplied from General Company for Production of Chemical Fertilizers.

**Adduct Formation**

During each experiment the reaction flask was heated and controlled by using a water bath with heater and thermostat as shown in figure 1. The flask also surrounded directly by a cooling coil which was used for cooling the flask contents. The oil fraction was mixed with the solvent and urea solution in the reaction flask at controlled specified temperature. Chilled water is pumped from the chiller into the cooling coil in order to reduce the temperature of the flask mixture from initial reaction temperature 52 ˚C to the final reaction temperature 30˚C at the desired time and mixer speed. At the end of each experiment the resulted complex was used for adduct separation unit.

**Adduct Separation**

The separation of the adduct from the dewaxed oil take place by vacuum filtration. The separation of oil-solvent phase and urea saturated phase was completed by separating funnel to separate the adduct crystals. Then these crystals is washed twice by using cold solvent (MEK + toluene) and then re-filtered.

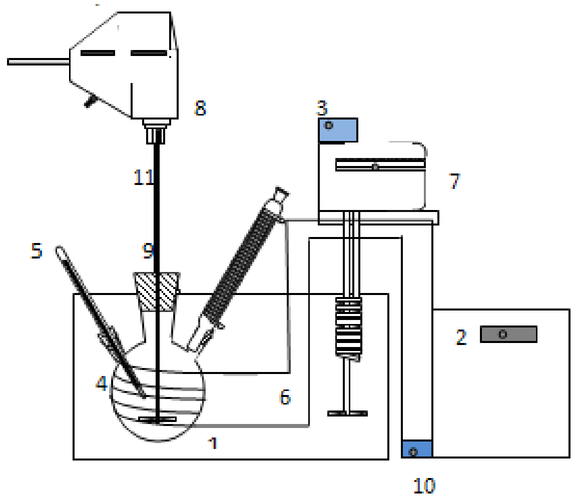

Figure 1 Schematic Diagram of the Laboratory Adduct Formation unit.

1. Water bath
2. Chiller
3. Thermostat
4. Reaction flask
5. Thermometer
6. Cooling coil
7. Heater with stirrer
8. Electric motor
9. condenser
10. pump
11. stirrer

### Adduct Decomposition

The adduct decomposition takes place at about temperature 80 ˚C to separate the wax from the urea dissolved in water.

### Solvent Recovery

The solvent was recovered from the oil-solvent mixture by simple distillation

### Pour Point determination

The pour point is the lowest temperature at which oil will move, pour, or flow when it is chilled without disturbance under definite conditions [3]. ASTM D97 was used to determine the pour point. The oil sample charged in a special tube and cooled, by using a succession of baths at ever lower temperatures [14], the pour point of a sample is determined to be 3 ˚C above the point at which a sample can be horizontally held and no movement occurs for five seconds[4].

## Results and Discussion

### Effect of Mixing Time

Figure 2 shows that the pour point against mixing time at different solvent/oil ratio, while Figure 3 shows the pour point against mixing time at different urea/wax ratio. Figure 2 indicate clearly that the pour point of dewaxed oil decreases with increase in solvent/oil ratio. The same trend of pour point is observed as urea/wax ratio increases, as shown in Figure 3.

The small increments in the pour point after 40 min may be due to the consumption of all the solvent through reaction and its no more reaction can occur between the feed stocks and the urea.

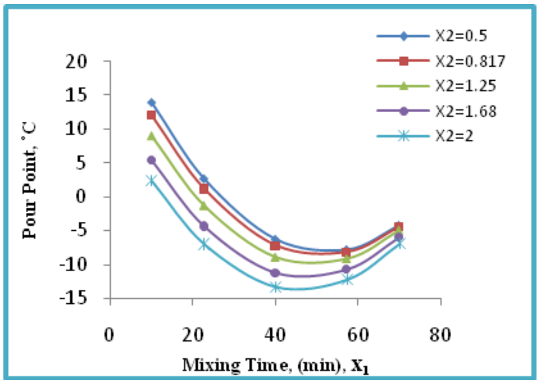

Fig. 2 Effect of the mixing time on the pour point at different solvent/oil ratio.

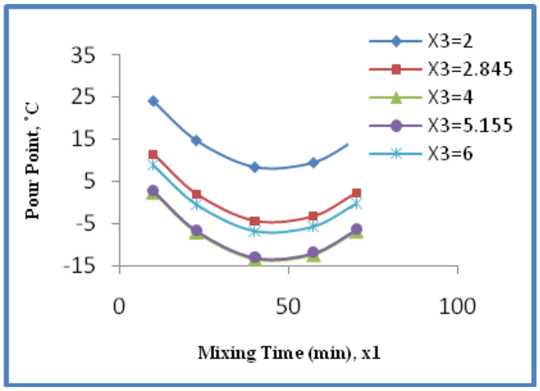

Fig. 3 Effect of the mixing time on the pour point at different of urea/wax ratio.

### Effect of Solvent/ Oil (vol. /vol.)

Figure 4 shows that the pour point against solvent/oil at different of mixing time, while Figure 5 shows that the pour point against solvent/oil at different of urea/wax.

It can be seen from Figure 4 that the pour point of the dewaxed oil decreases as solvent/oil increase at different mixing time. The same trend of the pour point of the dewaxed oil decreasing is observed as urea/wax increasing as shown in Figure 5. This decreasing in the pour point may be to the change in the equilibrium between straight-chain hydrocarbon and urea that influenced by increasing of the ketone solvent, as also stated by Bailey and co-workers [15], that found the solvent to feed ratio was to be important and it was necessary to maintain a sufficient solvent rate to the filter to effect adequate washing of the filter cake.

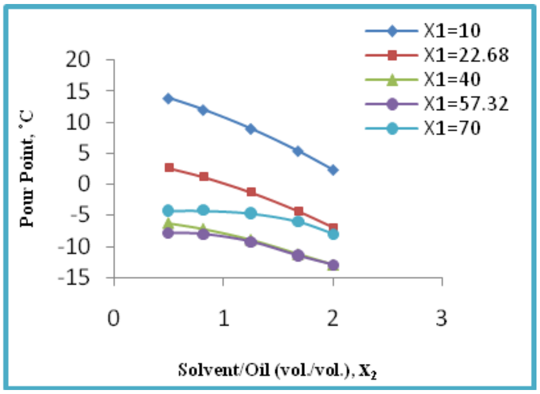

Fig. 4 Effect of solvent/oil (vol. /vol.) on the pour point at different mixing time.

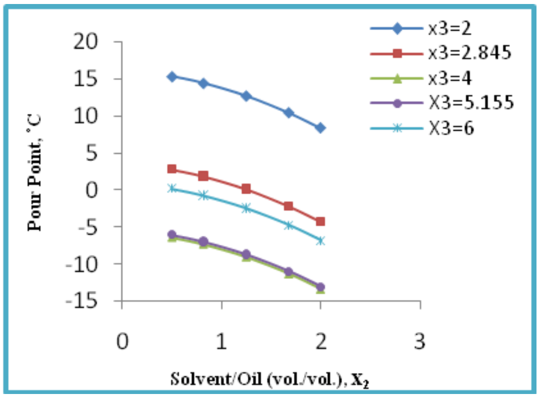

Fig. 5 Effect of solvent/oil ratio on the pour point at different urea/wax ratio.

### Effect of Weight Ratio of Urea/Wax.

Plot the pour point of the dewaxed oil against urea/wax at different mixing time is shown in Figure 6, while Figure 7 shows that the pour point of the dewaxed oil against urea/wax at different solvent/oil.

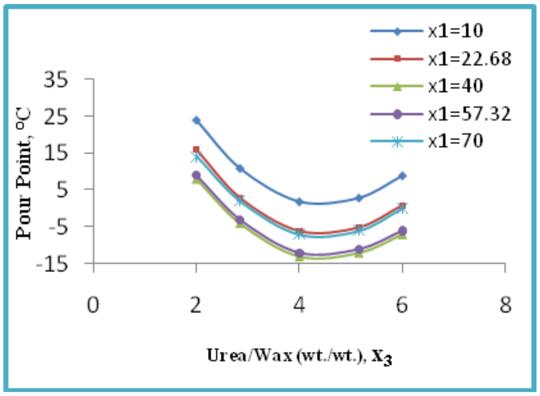

Fig. 6 Effect of urea/wax on the pour point at different mixing time.

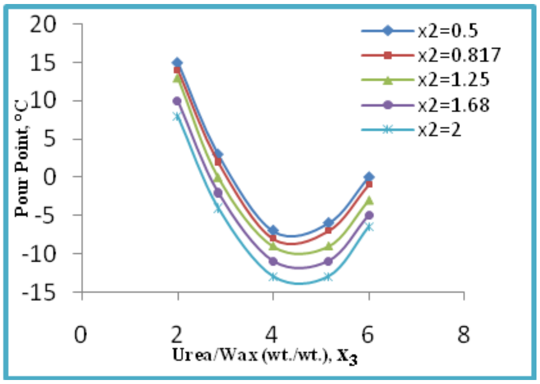

Fig. 7 The effect of the weight ratio of urea/wax on the pour point at different solvent/oil.

Figure 6 indicate that the pour point of the dewaxed oil was reduced with urea/wax increase up to 4 at different mixing time and solvent/oil volume ratio 2, and slightly increase in pour point occurs above 4 ratios.

The same trend of the pour point of the dewaxed oil decrease is observed as urea/wax increases as shown in Figure 7. According to the data taken from literatures [7,16,17], the stoichiometric amount of urea required to form an adduct with n-paraffin is about 3.5 gram of urea for each gram of n-paraffin. Due to that using quantity of urea lower than the stoichiometric amount (deficient urea) leads to extract less n-paraffin and produces less adduct crystals. Treatments with large amount of aqueous urea were avoided here because in this case mixtures of hydrocarbons and an aqueous phase are difficult to separate.

## Conclusions

The possibility of studying urea dewaxing of lubricating oil in four stages adduct formation, adduct filtration, adduct decomposition and solvent recovery. The recommended best conditions for pour point of the dewaxed oil were 40 min mixing time, 2 volume ratio of solvent/oil, and 4 weight ratio of urea/wax. At these conditions the pour point of the dewaxed oil decreased from 24 to -13 ˚C.

## References

1. Board N., "Modern Technology of Petroleum, Greases, Lubricants, and Petrochemicals", NIIR Project Consultancy Services (NPCS), India, 2004.
2. Gary J.H., "Petroleum Refining Technology and Economics", 4th ed., Marcel Dekker Inc., New York, 2001.
3. Speight J.G., "The Chemistry and Technology of Petroleum", 4th ed., CRC Press, Taylor and Francis Group, LLC, 2007.
4. Hsu C.S. and Robinson P.R., "Practical Advances in Petroleum Processing", 1, Springer Science and Business Media, Inc., 2006.
5. Kramer D.C., Lok B.K., and Krug R.R., Amer. Soc. for Testing and Materials, West Conshohocken, PA, 2001.
6. Hassan, N.M., Butterworth-Heinemann, Vol. 4, 62-64, 1994.
7. Marechal J. and Radzitzky P., J. Inst. Pet., 46 (434), 33 – 45 (1960).
8. Kunert, Maximilian, Sandhack and Lothar, U. S. Patent, 3847791, 1974.
9. Rogers T.H., Brown J.S., Diekman R. and Kerns G.D.,Oil and Gas J., Pet. Ref., 36 (5), 217 – 220, July (1957).
10. McKetta J.J. and Cunningham W.A, "Encyclopedia of Chemical Processing and Design", CRC Press, 15, 1976.
11. Yata N., Bulletin of the Japan Pet. Inst., 4, 35-44, 1962.
12. Mead T.C., and Wright J.H., U.S. Patent, No. 4504376, 1984.
13. Yasin S.R., "dewaxing of distillate oil fraction (400-500 °C) using urea", Ph. D. Thesis, submitted to the College of Engineering, University of Baghdad, 2005
14. Denis J., Briant J. and Hipeaux J.C., "Lubricant properties, analysis and testing", translated from the French by Dr. G. Dobson, published by Editions Technip, Paris, 2000.
15. Bailey M.A., Bannerot R.A., Fetterly L.C. and Smith A.G., Ind. Eng. Chem., 43 (9), 2125 – 2129 (1951).
16. Lakshmi D.S., Krishna M.R., Pet. Science and Tech., 15 (7-8), 685-697, 1997.
17. Kunert, Maximilian, Wegner and Hans-Georg, U. S. Patent, 3945912, 1976.