Degreasing and Solvent Regeneration in Metal Parts Cleaning using N-Methylpyrrolidone

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Introduction
N-Methylpyrrolidone (NMP) is a highly polar (4.09 D dipole moment) organic compound not readily miscible with saturated, straight chain hydrocarbons at room temperature (24 to 25 °C). Despite this fact, NMP does aid the dispersion and removal of burnt-on carbon deposits from metal surfaces. The large polarity prevents the pure solvent, alone, from effectively solvating and displacing some oils and greases at room temperature.

By raising the temperature of NMP to a range of 63 to 68 °C, oils of different viscosities become miscible in NMP (the mixtures evolve from two-phase systems at room temperature through a cloudy/hazy blend to a clear “solution” at 63 to 68 °C). Once the source of heat is removed from the oil/NMP blends, the “solution” returns to two-phase systems as it cools.

This property of polar and nonpolar compounds separating and becoming miscible as the temperature is raised and lowered, can be utilized in a system for metal parts cleaning. The NMP can be continually cleaned, or recycled, simply by lowering its temperature and allowing the oil to separate and rise to the surface to be skimmed away.

Discussion
After it was noticed that the undesirable hydrocarbons were miscible in NMP at elevated temperatures, it became readily apparent that this would be of no value in a metal parts cleaning process if the NMP/oil blend in the cleaning bath could not be removed easily from the surface of the metal.

Because NMP is almost instantly miscible in nearly all polar solvents, rinsing the NMP/oil blend with a polar solvent is the easiest way to “clean” the metal surface. All ketones, alcohols, and ethers would serve this purpose quite well and, in some cases, may be the rinse medium of choice. The most appropriate polar solvent for use as the cleaning rinse, from both safety and air quality standpoints, is water.

NMP is miscible in all proportions with water. A metal part is taken out of a hot NMP bath and placed in a hot water bath (or a series of water baths). The NMP/oil film on the metal surface dissolves in the water. The metal part exits the hot water bath with a clean surface having water droplets that must be removed by a drying process appropriate for the part. In the cleaning experiments presented here, a hot air oven was used as the means of drying the parts.

A separate set of experiments was carried out to determine the feasibility of reclaiming the NMP from the oils after the two compounds were in solution at elevated temperatures for extended periods. Most of the cleaning work was done in baths that were used at most for an 8-hour day, then discarded. In an actual production situation, the oil may not be cleaned out of the solvent bath that regularly. Also, because the oil and the NMP readily separated, and because NMP is not classified as a hazardous waste, the potential to re-use the oil, if it does not thermally break down, does exist.

In current vapor degreasing processes, the oils being removed and the cleaning solvents used are more miscible in each other than are NMP and oils. The potential for small amounts of these solvents to be left in the oil sludge that is to be discarded may change the classification of the waste oil sludge from non-hazardous to hazardous. If the waste oil sludge is non-hazardous, the presence in it of small amounts of residual NMP will not change the sludge waste classification to a hazardous rating.
Experimental Procedure

Part 1
The first experiments performed were to determine if NMP could effectively remove oils from metal surfaces as shown in Table 1, five different metal surfaces were cleaned. (Note: NMP is non-corrosive to metals, in its neat form, at the temperatures used in the cleaning process.)

<table>
<thead>
<tr>
<th>TABLE 1: PARTS CLEANED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass Valve fittings with (2) blind holes</td>
</tr>
<tr>
<td>Aluminum 3 in. long pieces of radiator core fluid pipe</td>
</tr>
<tr>
<td>Carbon Steel 4 in. long (3/8 in. diameter) threaded bolts</td>
</tr>
<tr>
<td>Stainless 1/4 in. diameter threaded rod with blind Steel hole in the end</td>
</tr>
<tr>
<td>Copper 3 in. long; 3/8 in. ID copper tubing</td>
</tr>
</tbody>
</table>

Parts Preparation
The means chosen for investigating the ability of NMP to remove grease from a part, was to examine the weight change of samples. To insure that the samples were as "soil free" as possible at the start, all samples were pre-cleaned as follows and weighed to the nearest 0.2 mg prior to the application of control soils. The soils used were shown in Table 2.

1. Six sets of parts were allowed to stand in beakers filled with DURÔ™ NAVAL JELLY® Rust Remover (a phosphoric acid-based, thickened metal cleaner), at room temperature, for 15 minutes.
2. After removal from the cleaner, the parts were rinsed and brush-scrubbed clean, using deionized water.
3. The parts were then quickly rinsed with acetone, then allowed to stand at room temperature and humidity before being weighed.

Application of Oils
The oils chosen for removal were of varying viscosities. The range covered was from water-thin to high-viscosity-index blend stocks.

1. The previously weighed parts were dipped into the various oils listed above, then let hang freely (for drip-off of excess oil) for 12 hours.
2. Parts were then placed into a forced air oven for 90 minutes at 80 °C, to ensure that any volatiles could be evaporated quickly, also to ensure full wetting of the metal surfaces by the warm oils.
3. After removal from the oven, the parts were allowed to stand at room temperature and humidity for 2 days before being weighed just prior to the NMP degreasing process. The soiled parts were again weighed to the nearest 0.2 mg.

<table>
<thead>
<tr>
<th>TABLE 2: SOILS</th>
</tr>
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<tbody>
<tr>
<td>DESCRIPTION</td>
</tr>
<tr>
<td>LPA-210 solvent Paraffinic, naphthenic solvent</td>
</tr>
<tr>
<td>Low Odor Paraffin Hydrotreated light distillate; ( C_{10}^{15} )</td>
</tr>
<tr>
<td>Solvent (LOPS) saturated hydrocarbons 97% — ( C_{10}^{15} ) aromatics 3%</td>
</tr>
<tr>
<td>MVI 60 SE Neutral Solvent refined; hydrotreated middle distillate</td>
</tr>
<tr>
<td>HVI 150 Neutral MQ Solvent refined; hydrotreated heavy paraffinic distillate</td>
</tr>
<tr>
<td>TELURA 323 Hydrotreated heavy naphthenic distillate</td>
</tr>
</tbody>
</table>
Cleaning Process
1. The cleaning bath was a 2000-ml Pyrex beaker filled with 1700.0 g of NMP. The bath was mounted on a hot plate/magnetic stirring apparatus, so that agitation could be supplied during the NMP cleaning stage. It was found that shorter dwell times were obtained when the NMP was agitated.
2. Bath temperature was maintained at 65 ± 3 °C. The stirring magnet was kept at a medium-to-slow speed.
3. The parts were manually placed in the NMP bath and remained there for two minutes.
4. The parts were then removed from the NMP bath and placed manually into a deionized water rinse bath maintained at 55 ± 3 °C. This bath, also in a 2000-ml pyrex beaker, was agitated at a medium/slow speed with a magnetic stirring apparatus.
5. Dwell time in the water rinse bath was 20 to 25 seconds.
6. After manual removal from the water rinse bath, any excess liquid water was blown off the parts with a stream of room-temperature dry nitrogen gas.
7. The parts were allowed to stand at room temperature for 30 minutes before preparation for final weighing.

Final Parts Weighing
1. The 30-minute room-temperature drying time was followed by 30 minutes in a forced-air oven at 70°C.
2. Upon removal from the oven, the parts were allowed to stand at room temperature and humidity for four hours in the same air-conditioned laboratory where the initial weighing was done.
3. The parts were then weighed to the nearest 0.2 mg.

Results
Six sets of parts were cleaned as described above. All of the parts (aluminum, brass, carbon steel, stainless steel and copper) from each set had final weights of 99.997 to 100.004 percent of their original weights.

The conclusion was that a process using NMP as a cleaning/solubilizing medium could be used to degrease metal parts.

Further experiments were carried out to determine the amount of various oils that could be present in the NMP bath before the cleaning process was impaired. Those oil loading levels are listed in Table 3.

![TABLE 3: NMP BATH OIL LOADING LEVELS (weight %)]

<table>
<thead>
<tr>
<th>OIL</th>
<th>LOADING LEVEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOPS</td>
<td>15-20%*</td>
</tr>
<tr>
<td>LPA-210</td>
<td>15-20%</td>
</tr>
<tr>
<td>MVI 60 SE</td>
<td>20-25%</td>
</tr>
<tr>
<td>HVI 150 NEUTRAL</td>
<td>5-6%</td>
</tr>
<tr>
<td>TELURA 323</td>
<td>5-6%</td>
</tr>
</tbody>
</table>

*At the lower end of the range the cleaning process was not impaired. At the upper limit, 0.5 to 1.0 percent increases in final weight were recorded.
Part 2
NMP Recycling and Separation from Oil
Once it was determined that NMP could be used to "solvate" oil and clean metal parts, separating the NMP from the oils was investigated in two areas: First, a series of tests were performed at room temperature to determine if the oils would be miscible with NMP in a percentage that would interfere with the cleaning operation. Second, although NMP is thermally stable at the operating temperature of the cleaning process, a set of experiments was run to determine the thermal stability of the oils in NMP. If the oils remain stable, it would allow a greater number of options for their re-use.

A series of NMP/oil blends was mixed at room temperature and poured into glass sample bottles that were tightly closed with polyethylene-lined caps. These blends are listed in Table 4.

<table>
<thead>
<tr>
<th>TABLE 4: NMP/OIL BLENDS (weight %)</th>
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<tbody>
<tr>
<td>COMPONENT</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>LOPS</td>
</tr>
<tr>
<td>LPA-210</td>
</tr>
<tr>
<td>MVI 60</td>
</tr>
<tr>
<td>HVI 150</td>
</tr>
<tr>
<td>TELURA 323</td>
</tr>
<tr>
<td>NMP</td>
</tr>
</tbody>
</table>

Heat Age
1. All of the NMP/oil samples were placed in a static air oven; temperature: 70 °C.
2. The blends were allowed to remain in this oven undisturbed for six days. The samples were then removed and allowed to cool to room temperature. (NOTE: All samples prior to being placed in the oven were two-phase systems, i.e., an oil layer on top of NMP. When the samples were removed from the oven, they were single-phase "solutions" that separated slowly as they cooled.)

NMP/Oil Separation
1. The NMP and oils separated approximately one hour after removal from the oven into room-temperature air.
2. Each sample was then poured into a separatory funnel and allowed to stand undisturbed.
3. Samples of the NMP layer (bottom) were taken after the NMP/oil blends had been undisturbed in the funnels for four hours. Second samples of the NMP layers were taken after standing undisturbed for 24 hours.

Analysis of Oil Layer
1. The remainder of the NMP layers were drained off, as well as a small portion of each of the oil layers, and discarded.
2. A known amount of distilled water was then added to each of the separatory funnels. The oil/water mixture in each funnel was shaken vigorously by hand for several minutes.
3. Each funnel was then allowed to stand undisturbed for four hours.
4. At the end of this time, samples of the water layers were drawn to be analyzed for NMP content. The remainder of the water layers and small portions of the oil layers were drawn and discarded.
5. Samples of the oil were drawn off and saved for analysis, following the taking of the water samples.

Results
Samples taken from NMP layer after initial separation of NMP/oil
Analysis was done by UV,* and with a GC-FID on a 0.25-μm SE-54 column. Analytical results are shown in Table 5.

a. LOPS was present in the NMP at 6.4% by weight.
b. LPA-210 was present in the NMP at 5.75% by weight.
c. MVI-60 was present in the NMP at 7.2% by weight.
d. NMP was present in the TELURA-323 at 600 ppm by weight*
e. NMP was present in the HVI-150 at 500 ppm by weight**

* Only oils a, b, c, and e have absorption bands in the UV.
** TELURA-323 and HVI-150 were essentially insoluble in NMP at room temperature.

There were no significant differences between those samples that stood undisturbed for four hours (before an NMP layer sample was taken) and the sample that stood undisturbed for 24 hours.

Samples of oil rinse water
NMP/oil was separated, then the oil layer was rinsed with known amounts of water. All samples were analyzed by GC-FID on a 0.25-μm SE-54 column. Analytical results are shown in Table 6.

a. Analysis of NMP in the water supported the data that LOPS is soluble in NMP at a 6.4% level (samples 1, 2, 3, 4).*
b. Analysis of NMP in the water supported the fact that LPA-210 is soluble in NMP at a 5.75% level (samples 5, 6, 7).
c. Analysis of the NMP in water supported the fact that MVI-60 is soluble in NMP at a 7.2% level (samples 8, 9, 10).
d. Analysis of the NMP in water showed that NMP was soluble in HVI-150 at a 600 ppm level. (Samples 11, 12, 13)**
e. Analysis of the NMP in water showed that the NMP was soluble in the Telura-323 at a 500 ppm level (samples 14, 15, 16)**

* Samples (3) and (4) (NMP and oil mixture) were single-phase at room temperature.
** Telura-323 and HVI-150 were essentially insoluble in NMP at room temperature.

Samples of oil layer taken after water rinse
The remaining oil was analyzed after water rinse of oil. All samples were analyzed by GC-FID on a 0.25-μm SE-54 column. Samples were diluted with heptane to 5% (oil wt.) for injection.

a. There were no changes in any of the oil "finger prints" with six-day heat aging.
b. The NMP concentrations in all of the oil samples analyzed were below the limit of detection.
Conclusions
The initial experiment supports the hypothesis that saturated hydrocarbon oils can be removed from metal substrates, using a process having NMP as a cleaning agent. The second experiment yielded the following results:

1. NMP has no degrading effect on the oils when in contact with them for extended periods at 70°C; the oils, therefore, should not be degraded at the stated cleaning temperature of 65 °C.
2. The various oils separated fairly quickly from the NMP. The lighter oils, LOPS, LPA-210 and MVI-60 did not separate completely. At room temperature, however, the wt. percent of oil soluble in the NMP was far below the levels necessary to interfere with effective cleaning.
3. The GC analysis of the oils that were collected and washed with water showed that oils could be "cleaned" of NMP by washing them with water.

The three facts brought to light by the second experiment, in conjunction with the initial cleaning experiment, suggest development of an NMP cleaning process that would allow continual reuse of the NMP. Oil could be skimmed from the surface of the NMP on a daily basis, if desired, yielding a regenerated bath.

The facts that the oils are not degraded, and that the NMP is easily removed from the oils with water, suggest the potential of reclaiming and re-using the oils.

Further work is underway to prove feasibility of such a cleaning process on a larger scale.

Acknowledgments
The analytical work was carried out by a BASF Research Services laboratory located in Wyandotte, Michigan. GC work done by Hulya Ahmed and Steven Springer-Wilson. UV work done by William V. Floutz, and L. Barczewski.

Proposed Process for Using NMP as a Metal Parts Cleaning Medium: (See Figure 1)

A. NMP Bath:
   - Agitated with spray under immersion
   - Maintain temperature at 63 ±3 °C.
   - Dwell time in bath: 2 minute

B. NMP re-cycle/separation system:
   - Continually draw off some of the NMP/oil mixture from the cleaning bath.
   - Cool down drawn off fluid (quickly) in a small heat exchanger.
   - Fluid enters small separation tank just under the surface of the oil/NMP interface.
   - NMP continually (and slowly) drawn from the bottom of separation tank and returned to the cleaning bath.

C. Air Knife: Blow excess NMP from the parts, back into NMP bath. Minimize drag-out losses.

D. "Clean Water" Rinse Station: Because the water is heated and agitated, in lab trials it was found that the water rinse bath has 0.05 to 0.1 percent by weight of NMP/oil present and, although a little hazy in appearance, still provides clean parts. For spot-free parts, distilled water that is run through a membrane, to separate out the bulk of the oil/water rinse, is required as the "clean water."
   - Temperature of bath: 55 ±3 °C.
   - Dwell time in bath: 30 to 45 seconds.
   - Water is agitated with spray under immersion mechanism.

E. Rinse Water/NMP Oil Separation Module
NMP is water soluble, and not readily taken out of water with ion exchange resins. As the concentration of NMP builds up in the rinse water, it may have a tendency to solubilize or emulsify the oil or slow the
drying process. A vacuum still efficiently separates the water from the NMP. There are no azeotropes formed, thus yielding pure water.

F. Air Knife: To blow off excess water that is carried out of the rinse station. This will aid in speeding up the process.

G. Drying module

H. Method to Trap or Minimize NMP Air Emissions

NMP has a fairly low vapor pressure at room temperature (0.24 mm Hg). This increases at 63 to 68 °C and some amount of solvent will evaporate (See Figure 2). The amount of NMP that physically leaves the work facility as a VOC can be minimized by either passing exhaust air through a water wash scrubber (recall miscibility of NMP in water), or through a bed of activated carbon.

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**Figure 1: Proposed NMP Metal Cleaning Process**

**Figure 2: NMP Evaporation** (for experimentation details see appendix A)
APPENDIX A
68 °C Evaporation Experiment: (two different trials)
1. 600-ml beaker; 450.0 g NMP added to beaker.
2. Bath agitated at medium to low speed with a magnetic stirrer for entire length of experiment.
3. No cooling coils placed either directly above the beaker or in the beaker above surface of solvent.
4. Trials were run inside a hood with exhaust turned on and air flow through the hood of 180 cubic ft. per minute.
5. Trial duration: 4.5 hours.

Room Temperature (24 °C) Evaporation Experiment
1. 21.0 g NMP were poured into a petri dish (dimensions 3.375 in. ID by 0.50 in. in height).
2. The dish was placed on an analytical balance that measured to the hundredth of a gram.
3. The balance was placed under a hood, but no exhaust was turned on: totally static air.
4. The read-out from the balance was observed from time to time during an approximate 2 hr. and 10 minute period. No change in the read-out was noted.

APPENDIX B
Physical Properties of N-methyl pyrrolidone
Molecular weight: 99.1
Boiling point: 203 °C (397 °F)
Flash point: 91 °C (198 °F)
Specific heat (liquid):
   0 °C: 0.401 cal/g
   50 °C: 0.465 cal/g
   100 °C: 0.502 cal/g
Specific gravity: 1.027 to 1.03 g/cc (at 25 °C)
Weight per gallon: 8.58 lbs.
Viscosity at 20 °C: 1.7 centipoises
Heat of vaporization (at 100 °C): 122 cal/g (219 BTU/lb)
Heat of combustion: 7.29 kcal/g (13,100 BTU/lb)

Calculated Energy Requirements for Heating and Maintaining an NMP Bath (for 8-hour shift)

Assumptions
1. 75 gal NMP are in a 37 x 24 x 24 in. (hwl) steel container. The open top and steel-walled sides are all in contact with air at room temperature.
2. Liquid-to-air heat flow: 1.8 BTU/hr/ft²/°F, AT
3. Liquid-through-metal-to-air heat flow: 10 BTU/hr/ft²/°F, AT

Amount of energy to heat 75 gal from 25 to 65 °C
\[
\Delta T = 40 \degree C
\]

75 gal NMP = 291,468.0 g NMP
291,468.0 g NMP x 0.47 cal/g x 40 = 5.48 x 10⁶ cal
5.48 x 10⁶ cal/(252 cal/BTU) = 21,800 BTU

Amount of energy lost to air
Room-temp. air: 76 °F; Liquid: 149 °F
1. Directly to air: 1.8 BTU x 4 ft² x 73 °F ΔT = 5256 BTU/hr
2. Through metal to air: 5 sides x 6.16 ft²/side =
   30.8 ft² x 10 BTU/hr x 73°F ΔT = 22,500 BTU/hr
   27,800 BTU/hr x 8 hrs = 216,000 BTU/Day
Total = 216,000 BTU + 21,800 BTU = 237,800 BTU/Day