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CLEANER FOR AUTOMOTIVE COOLING SYSTEM

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1 Claim. (Cl. 252—138)

This invention relates to aqueous alkaline detergent compositions and more particularly is concerned with package-stable detergent compositions adapted for use in cleaning automobile radiators and to method of preparing same.

In view of the relatively small fluid capacity of the cooling or heat exchange system of an automobile, it is important that the system operate at maximum efficiency to prevent loss of the fluid which can cause overheating and consequential damage to the engine. It is desirable that the system be periodically cleaned or purged to remove loosely bound rust, corrosion products, grease and oils before the detrimental deposits become tightly bound and present the probability of flaking off and clogging of the radiator.

There is a distinct need for a liquid detergent concentrate which can be added to the automobile cooling system in small volume to be diluted many times and which in the diluted condition serves as an efficient cleaner when circulated in the system for a period as short as 30 minutes and which can remain in the system for a period as long as 24 hours without harmful effects.

An important requirement of the liquid detergent is that it must be substantially non-foaming, otherwise foam-formation would cause significant loss of coolant from the system while the cleaning operation was being carried out during normal operation of the vehicle.

Other important requirements desired by the user are that the detergent concentrate shall be a liquid for convenience in introducing it into the radiator and it shall be sufficiently concentrated that a dosage of 12 or 16 fluid ounces of the detergent concentrate is adequate for cleaning an automotive cooling system of average capacity. The liquid detergent concentrate should be package-stable over a wide temperature range as the supplier or the user may store the detergent concentrate where temperatures ordinarily range from sub-zero to 150° F. and higher. Often the precipitated components of aqueous detergent compositions are not easily redissolved after freezing and thawing, particularly the sodium salts. No special treatment should be required to restore the aqueous concentrate to its original useful condition after thawing.

It is a general object of this invention to provide a detergent concentrate having the above described desirable requirements. A more specific object is to provide an aqueous alkaline detergent concentrate for use as an additive to the aqueous coolant of an autombile cooling system, which concentrate on 20 to 60 fold dilution is an efficient cleaner for rapid dispersion of rust, corrosion products, oils and grease and is non-foaming during normal operation of the vehicle. Another important object is to provide an aqueous detergent concentrate which after dilution to the operative range of concentration for cleaning does not require chemical neutralization in its elimination from the system, residual cleaner remaining after normal draining of the system

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and diluted by filling the system with water being innocuous to the metal and rubber parts of the cooling system. A further important object is to provide an aqueous detergent concentrate comprising a salt which redisperses upon thawing of the composition without agitation of the liquid composition. Other significant and important objects will become readily apparent as the description of the invention proceeds.

The objects are accomplished by preparing an aqueous liquid alkaline detergent concentrate by dissolving in water potassium silicate, potassium chromate and potassium salts of orthophosphoric acid or equivalently the salt-forming components of the aforementioned salts, and a water-soluble salt of the polymeric condensation product of naphthalene sulfonic acid and formaldehyde.

The following example represents the best mode contemplated for practicing the invention and the illustrative example is not to be construed as being restrictive in scope except as specifically limited in the appended claim.

Example

	Percent by wt.
Water	56.25
Potassium hydroxide	13.20
Phosphoric acid	6.85
Chromic anhydride	2.15
Potassium silicate solution	17.75
Sodium salt of the polymeric reaction product of naphthalene sulfonic acid and formaldehyde ("Tamol–N")	3.80
	100.00

The potassium hydroxide was the commercially available 85% grade, low in chloride content, the chloride content being less than that corresponding to 0.5% as KCl.

The phosphoric acid was the commercially available 85% (N. F.) National Formulary grade.

The chromic anhydride was the commercially available grade which was of at least 99.5% purity.

The potassium silicate solution was a commercially available aqueous silicate solution containing an amount of silicate corresponding to 12.6% K_2O and 26.5% SiO_2 by weight, the weight ratio of K_2O/SiO_2 being about 1:2.10. The molar ratio was about 3.3 mols of SiO_2 per mol of K_2O.

The sodium salt of the polymeric condensation product of naphthalene sulfonic acid and formaldehyde was essentially a mixture of approximately equal parts of dinaphthylmethane disulfonic acid and the corresponding trimer containing three naphthalenesulfonic acid groups per molecule, with small proportions of the higher polymers containing as many as 8 naphthalene sulfonic acid groups per molecule. Proprietary products which are useful in this invention in addition to "Tamol–N" include "Tanak A," "Daxad–11," "Darvan–1," and "Blancol." The potassium salt of the polymeric condensation product of naphthalene sulfonic acid and formaldehyde can be substituted on a pound for pound basis for the sodium salt. In the aqueous composition of the above example, the potassium salts correspond to the approximate molar proportions of:

K_2O	1.000
H_3PO_4	0.480
CrO_3	0.174
SiO_2	0.632

The anionic components are in the approximate molar proportions of 3 mols H_3PO_4, 1 mol CrO_3 and 4 mols SiO_2.

The salt-forming components of the example were added to the water in the order shown, initially forming a dilute solution of potassium hydroxide and thereafter the potassium hydroxide reacted with the phosphoric acid and chromic anhydride. As a safety precaution, mixing was carried out in a jacketed mixer with cooling water circulating through the jacket, the temperature of the composition preferably being maintained below about 100° F.

The composition of the example is an amber colored, clear, low viscosity liquid. The pH of the composition is about 11.1.

In order to test the effectiveness of the detergent composition in an automobile cooling system the following test was carried out which simulates the conditions which ordinarily exist in an automobile cooling system.

The liquid detergent concentrate was diluted with water to about 3% of its original concentration which corresponds to addition of 16 fluid ounces of the concentrate to a cooling system having a capacity of about 16.5 quarts. A brass plate having a shallow groove of about one square inch in area and about one/sixteenth of an inch deep filled with a weighed amount of synthetic rust/grease mixture was suspended in a bath of the diluted detergent. The bath was thermostatically controlled to a temperature in the range of about 170° to 180° F. and the bath mildly agitated by blowing air through the liquid. After the desired cleaning period, the brass plate with the adherent residual rust/grease mixture was removed from the bath and weighed to determine the loss of rust/grease composition. The rust/grease composition was a 50/50 uniform mixture of white petroleum and ferric oxide.

In carrying out the simulated cleaning operation described above, 50 ml. of the liquid detergent composition of the example were diluted to provide the cleaning composition. During a 60 minute cleaning period, 0.28 gram of the rust/grease mixture was removed from the suspended brass plate and dispersed in the cleaning composition.

In another test sample specimens of steel, cast iron, copper, brass and aluminum, representative of metals ordinarily used in an automotive cooling system, were electrically coupled as ordinarily found in the system and immersed in a bath of the aerated dilute cleaning composition of the example. The metal specimens were examined periodically after immersion in the cleaning composition and there was no significant corrosive attack on the metal during 5 days' immersion.

In carrying out evaluation of the cleaner under actual operating conditions, one pint quantities of the liquid detergent concentrate were added to a number of automobile cooling systems in which the fluid capacity ranged from about 10 quarts to about 22 quarts and operating temperature was controlled by thermostats opening at about 140° to 170° F. The cleaning cycle ranged from about 30 minutes after the thermostat opened to about 24 hours. During the cleaning period some automobiles had been driven up to about 200 miles under normal operating conditions. After the cleaning cycle, the cooling system was drained, filled with water and redrained. Draining of the system ordinarily removes only a major portion of the fluid from the system. While the residual spent cleaner after the first draining further diluted by filling the system with water can remain in the system without hazard, it is preferred to flush the residual cleaner from the system, particularly when the initially drained liquid is significantly discolored with rust. In such instances, flushing was accomplished by filling the system with water after the initial draining and redraining, repeating the operation several times if necessary until the drain water was clear. Alternatively, water can be introduced continuously to flush the system until the effluent water is clear.

Where the system to be cleaned contained alcohol-type or glycol-type anti-freeze, the system was drained of the anti-freeze and filled with water prior to addition of the detergent concentrate.

In all of these practical tests, cleaning action was efficient, there was no foaming and the operation was convenient, simple and rapid. Flushing equivalent to one fill of the system with water followed by draining and a refill with water was found to be ordinarily adequate. Neutralization of residual cleaner in the system was not required even when the flushing step was omitted and the normal undrainable content of the system was merely diluted with water to the normal volume of the system. At this dilution and at greater dilution associated with simple flushing, the aqueous coolant finally remaining in the system was mildly alkaline and desirably in the pH range of about 7.2 to 8.5.

The liquid detergent concentrate packaged in conventional tinplate containers having a coating weight of 0.5 pound of tin was package-stable and non-corrosive toward the interior surface of the container when stored for a period as long as nine months at atmospheric temperature ranging from about 65° F. to 100° F. Accelerated tests conducted in an oven at 120° F. for nine months also indicated excellent package-stability.

Package-stability or freeze-thaw resistance at temperatures below the freezing point of the concentrate were more significant. Packages of the liquid detergent concentrate subjected to three freeze-thaw cycles with exposure for 16 hours at 0° to 4° F. followed by thawing during storage for 4 to 6 hours at about 77° F. showed that the composition was freeze-thaw resistant and package stable under freezing conditions. Solid matter formed during freezing thawed to liquid condition without agitation. In contrast, a similar composition formulated with equivalent amounts of the corresponding sodium salts substituted for the potassium salts of the example was poor in freeze-thaw resistance. The sodium salts precipitated during freezing redissolved slowly, requiring mechanical agitation and heating to effect solution of the salts.

When substantial proportions of the sodium salts are in combination with the preferred potassium salts, the product continues to show the deficiency in freeze-thaw resistance. It is not necessary that sodium salts be entirely absent from the composition, but the significant advantages residing in the use of the potassium salts are diminished to less than a practical advantage when the potassium ion is decreased to below about 90 mol percent of the total mols of alkali metal present in the composition. It is preferred that the potassium represents at least 95 mol percent of the total alkali metal. The sodium ion contribution of the water-soluble surface active salt is insignificant, however the potassium salt of the polymeric condensation product of naphthalene sulfonic acid and formaldehyde can be substituted for the sodium salt of the example.

While ammonium and amine salts of the polymeric condensation product of naphthalene sulfonic acid and formaldehyde are also useful substitutes for the sodium salt specified in the example, the presence of these ammonium salts is less desirable because of potential corrosive attack on copper and copper-containing metals, such as brass. However, the useful concentration of surface active ammonium salts of the dilute cleaner remaining in the system for as long as 24 hours exhibits no significant corrosive attack on copper.

Although the example shows in situ formation of the pertinent phosphate and chromate salts, equivalent proportions of potassium orthophosphate and potassium chromate can be substituted for the salt-forming constituents.

While potassium silicate having a molar ratio of about 3.3 mols of SiO_2 per mol of K_2O is preferred, other commercially available grades of potassium silicate in which the molar ratio of K_2O/SiO_2 is in the range of 1:1 to 1:4 can be used. The mixture of the potassium salts represents 20% to 30%, based on weight of the packaged concentrate and corresponds to the following molar proportions:

K_2O	1.00
SiO_2	0.60 to 0.70
H_3PO_4	0.45 to 0.50
CrO_3	0.15 to 0.20

It is preferred that the mols of SiO_2 approximately equal the total mols of H_3PO_4 and CrO_3.

The content of the water soluble salt of the polymeric condensation product of naphthalene sulfonic acid and formaldehyde is not significantly critical. A content of at least 1% based on the weight of the aqueous concentrate is required to provide a practical improvement in the speed of dispersing rust and grease in the aqueous solution. The preferred amount of the surface active agent is in the range of 2% to 5% based on the total composition. No practical advantage was seen in using an amount greater than about 7.5%, based on total composition.

While the presence of the preferred amount of the surface active agent significantly enhanced the speed of the cleaning operation to the extent that cleaning was efficiently accomplished in a period as short as 30 minutes, the surface active agent within the same concentration range used as the sole cleaning agent in the absence of the pertinent mixture of phosphate, silicate and chromate salts, was inefficient in its operation and impractical as a cleaner for the intended purpose.

For a practical dosage of either 12 fluid ounces or 16 fluid ounces of detergent concentrate for an automobile cooling system of average capacity, 100 parts by weight of the liquid detergent concentrate preferably contains from about 20 to 30 parts by weight of the mixture of phosphate, chromate and silicate salts. The concentrate can be proportionately lower in salt content when the dosage is one quart instead of one pint, but packaging a dosage of this larger size at the lower concentration is not economical. The dosage of 12 to 16 fluid ounces in an automobile cooling system ranging in capacity from 10 to about 22 quarts corresponds to dilution of the concentrate from about 20 times to about 60 times the original volume. The concentration of the mixture of phosphate, chromate and silicate salts preferably is in the range of about 0.5% to 1.5% based on the weight of the diluted

cleaning solution. In cooling systems of higher capacity, it is desirable to increase the dosage to two 12 to 16 fluid ounce units in order that the concentration on dilution is preferably within the indicated range of salt concentration.

This invention provides a significant advance in liquid alkaline detergent concentrates adapted for use on 20 to 60 fold dilution as a non-foaming cleaning composition for efficient removal of rust, corrosion products, oils and greases from an automotive cooling system. The cleaner can be used while the automobile is in normal operation. Flushing to counteract the concentration of spent cleaner can be minimized, the object of flushing being primarily to eliminate dispersed rust, oils and grease rather than to dilute the residual spent cleaner. Chemical neutralization of the spent cleaner is not essential.

While there are above disclosed but a limited number of embodiments of the structure, process and product of the invention herein presented, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed, and it is desired therefore that only such limitations be imposed on the appended claim as are stated therein, or required by the prior art.

I claim:

An aqueous detergent concentrate adaptable as a cleaner for an automotive cooling system on dilution to 20 to 60 times its original volume, comprising the following approximate composition:

	Parts by weight
Water	56.25
Potassium hydroxide, 85%	13.20
Phosphoric acid, 85%	6.85
Chromic anhydride	2.15
Potassium silicate solution containing 12.6% K_2O and 26.5% SiO_2	17.75
Sodium salt of the polymeric reaction product of naphthalene sulfonic acid and formaldehyde	3.80
	100.00

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