

CAR WASH OPERATIONS AT SERVICE STATIONS AND OTHER CORRESPONDING FACILITIES

**Detergents, wash methods and
waste water treatment technologies**

Introduction

Finnish road conditions in the winter render cars dirty very fast, and powerful detergents are necessary to wash off the layers of dirt built up of gravel, slush, road salts and especially the bitumen fractions that studded tyres tend to strip off the roads. Typical problems for the Finnish summer driving conditions are insects and tree saps. In addition, metal dust grinding off the brake discs tends to stick to the wheel rims discolouring them yellow.

By washing the car regularly, car body corrosion can be prevented and the useful life of the vehicle can be extended. A layer of dirt on the vehicle paintwork conducts humidity into the pores of the paint and additionally it slows down the drying process of the surface. Moreover, a dirt layer tends to cover up eventual paint damage caused by flying stones and makes it more difficult to catch the damage in time for repair. Dirty windscreens, naturally, also impair the visibility in traffic.

Mechanized (automated) car wash is one of the services commonly provided by service stations. The effluents from a car wash facility often make up a significant proportion of the service station waste waters. Other effluents at service stations are conventional sewage waters and oily surface waters from the service station site. The chemicals used in car washing operations may present a hazard to the environment if they are released uncontrollably. In high concentrations, they may also impede the functioning of the general sewage and the waste water treatment processes.

Ever since the 1970s, the Finnish Petroleum Federation have maintained and managed these regulations and the Service Station Waste Water Programme. The purpose of the Waste water Programme is to ensure that the waste waters from service station car wash facilities do not interfere with the biological waste water treatment at the waterworks. The testing and authorisation procedure for car wash detergent mixtures constitutes an intrinsic part of the Service Station Waste Water Programme, and it also influences the contracts related with connecting to the sewage systems. The use of duly authorised chemicals also enhances service station occupational safety. The Finnish SFS standard 3352 Palavien nesteiden jakeluasema (combustible liquid distribution stations) refers to the Service Station Waste Water Programme and stipulates that the detergent mixtures used in vehicle washing operations must be duly tested and authorised. The system ensures that risk management is an essential part of responsible service station operations in Finland.

Further provisions on placing detergents on the market and on their use are laid out in the EU Detergent Regulation (648/2004/EC), the REACH Regulation (1907/2006/EC) and the CLP Regulation (1272/2008/EC). All amendments and changes made to the relevant legislation must naturally be observed in all car wash operations.

Discharge of harmful oleiferous waters from vehicle washing operations (automated and self-serve car washes) into the general sewage network can be prevented by using effective oil separators and duly tested and authorised detergent mixtures (testing is required only for detergents and detergent mixtures containing petroleum hydrocarbon solvents). The oil separation test verifies the speed of separation of the petroleum hydrocarbon solvents and the oil residues coming from the vehicle surfaces in the oil separator.

The chemicals used in self-serve car washing correspond with those used in automated car washes. The significant difference between these two car wash modes is that the solvents are appropriately recovered and forwarded for treatment in the controlled car wash systems, while

at the self-serve car wash sites, the oleiferous waste waters generally end up in the soil or in the general sewage network.

This manual contains information that is needed in managing waste waters from vehicle washing, for instance information on equipment, on car wash chemicals, on their authorisation procedure and on waste water treatment at the car wash facilities. Additionally, these instructions specify the requirements of the Finnish Petroleum Federation and its member companies on car wash chemicals.

Part D1 of the National Building Code of Finland (Water supply and drainage installations for buildings, Regulations and guidelines) confirms the special design of the oil separation structures defined in the instructions.

This manual is intended for use by:

- ▶ commercial car wash operators (oil companies, retailers, other car wash entrepreneurs)
- ▶ designers
- ▶ detergent manufacturers, importers and marketers
- ▶ local government environmental authorities
- ▶ regional rescue departments
- ▶ building control authorities
- ▶ water works professionals responsible for waste waters and industrial waste waters.

This manual is also intended for use by municipal authorities who are responsible for the inspection and approval of sewage planning, for the health and environmental supervision of car wash operations, and the supervision of the sewage systems.

The current eight edition of the manual contains significant amendments over the previous edition. In the current edition, all amendments made to the legislation and to building specifications have been observed and the chemicals approval criteria brought up to date. Subsequently, Annex 3 introducing some water reuse technologies has been appended to the manual.

The updated instructions were circulated for comments and the opinions expressed upon them have been duly taken into consideration. In September 2011, the Finnish Petroleum Federation ratified the updated instructions, and they must be observed by service stations and in the authorisation of detergents as from the first of January, 2012. All detergent authorisations issued on the basis of the previous edition of the instructions are in force up to the 31st of December, 2012.

1. Summary

Significant quantities of waste water are generated in car wash operations. Therefore, special attention needs to be paid to the car wash arrangements, the wash chemicals used and the treatment of the effluents from the car wash operations.

Automated car washing constitutes the bulk of all vehicle washing. A programmed car wash automate runs all the cycles of the wash without immediate intervention of the site staff.

Some motorists still prefer manual car wash by hand, which is often performed with the same chemicals as in automated car wash. Manual cleaning is used also to wash the engine, for which stronger washing chemicals are generally used.

A large selection of vehicle washing chemicals is available on the market. Solvents are used to dissolve grime, either as such or mixed with car shampoos. Presoak detergents and shampoos help remove the dirt from the car surfaces, and waxes are used to protect the surfaces against dirt. Surface active agents (also called surfactants or tensides) are generally the active agents in car shampoos, rinses and waxes.

The oleiferous waste waters from car wash facilities must be treated before leading them into the municipal drainage system. The wash waters are run from the site through a sand separator to an oil separator. The oil content of the aqueous phase in the oil separator and the quantity of oil ending up in the general sewage system depend, among other things, on the retention time of the effluents in the oil separator. The decomposition of the emulsion again is dependent on the properties of the solvent, the emulsifying agent and the detergent mixture. Special attention must be paid to the treatment of wash waters because detergents generally contain emulsifying agents. The waste mixture of oil and solvent retained in the oil separator must be removed often enough and subsequently forwarded for hazardous waste treatment. No other waters should be run into the oil separator designated for wash water treatment as they may disrupt the functioning of the separator. A sampling and shutoff well must additionally be installed in the car wash after the oil separator. It will enable daily measuring and monitoring of the oil separator.

According to the Act on Water Services (119/2001), the discharge of waste waters into a public sewer network is permissible only under a special access contract concluded between the car wash operator and the water works laying down the detailed stipulations for the access. If no municipal sewage network exists, the requirements laid down in the decree issued on service station environmental requirements (444/2010) and the guidelines given by the municipal environmental supervisory authority must be followed in the treatment and discharge of waste waters.

Moreover, the groundwater pollution prohibition of the Environmental Protection Act (amended 86/2000) must be observed in all car wash operations. Harmful substances may not be discharged into the environment so that ground waters in an important ground water area would become hazardous for human health or so that the quality of the ground waters would be in any other essential way compromised.

The government decree on service station environmental protection requirements (444/2010) stipulates that if the waters from the oil separator are run into a sewage network or a closed well, these waste waters must be treated in a class II oil separator that complies with the standard SFS-EN 858-1 (hydrocarbon concentration of the exiting water is below 100 mg/l). If the waste waters are not discharged into a sewage network, they must be treated in a class I oil separator that complies with the standard SFS-EN 858-1 and that results in the exiting water's hydrocarbon content to be below 5 mg/l.

Standard SFS 3352 on petrol filling stations stipulates that only detergents authorised for car wash may be used for that purpose. A detergent mixture refers to a combination of washing agents that are used at the various phases of the washing process, for example solvents, shampoos, rinsing agents and waxes.

In the authorisation procedure, the composition of the detergent mixture is verified and tested if it contains petroleum hydrocarbon solvents. The special purpose testing method verifies the separation from the water phase of the detergent mixture's petroleum hydrocarbon solvents and the oil removed from the vehicle. The detergent mixture may not contain chlorinated hydrocarbons or other chemicals hazardous to the environment. On application, the authorised detergent mixtures are registered in a central register of detergents authorised for car wash purposes, and a certification identifier is issued for them. The central register of authorised detergents is maintained by the Finnish Petroleum Federation.

The authorisation procedure for detergent mixtures aims at cutting down the car wash effluent load at the water and sewage works. By using duly authorised washing chemicals as well as oil separators that are of sufficient capacity, the car wash operators minimize their waste waters discharged to the water and sewage works. These procedures also ensure that the waste water treatment systems at car wash facilities are actually efficient and easy to run and maintain.

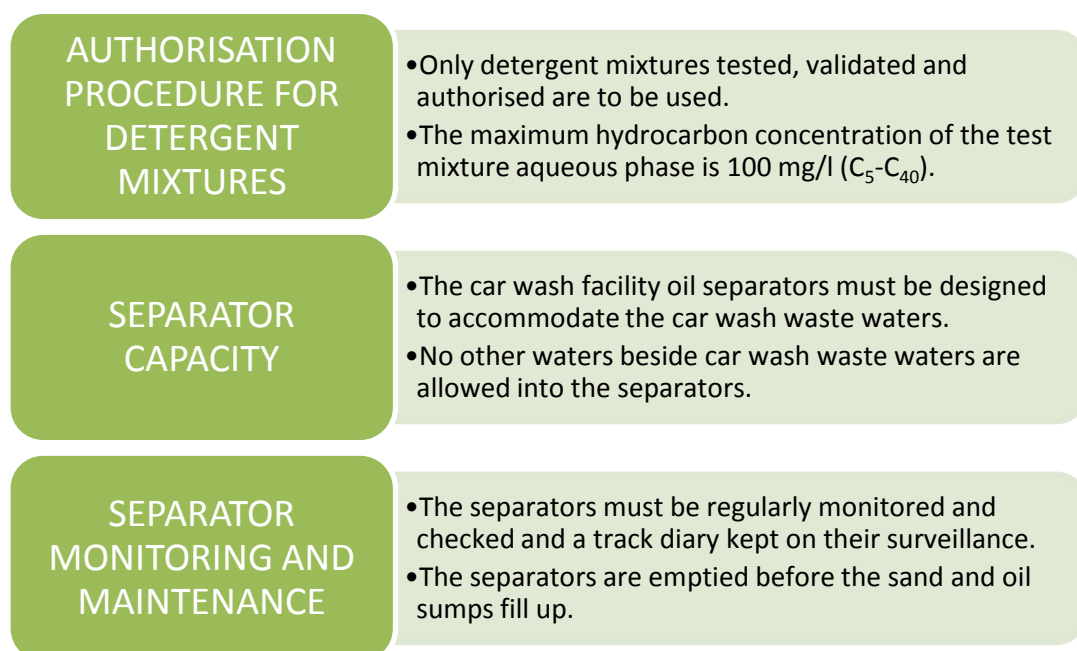


Figure 1 Service station waste water programme

The following steps make up the car wash waste water programme:

- 1) Only detergent mixtures authorised by the Finnish Petroleum Federation for car washing are used for that purpose. This restriction helps to inhibit the use of detergent mixtures and emulsifying agents that form non-degradable or persistent emulsions and contain other substances that have been classified dangerous for the environment.
- 2) The oil separators are designed so that the retention time of the car wash effluents is sufficiently long in comparison with the time required by the degradation of the emulsion.
- 3) The sand separator and the oil separator are systematically monitored and serviced, and a diary is kept of their function. The waste oils and the solvent mixture must be removed from the oil separators at frequent enough intervals.

The operator of the car wash facility is responsible for the waste water programme at the car wash site.

Additionally, other liquid waste also emerges from service station operations, the key ones being used motor oils, radiator fluids and battery fluids. All mentioned substances are classified as hazardous waste and must be disposed of and treated appropriately.

The instructions issued on service station waste management can be found in the publication named "Service station waste management" published by the Finnish Petroleum Federation.

Various types of small scale waste water treatment technologies have been developed for treating car wash waste waters. In Finland, water reuse has not gained much ground at commercial car wash operations or corresponding facilities. There are a number of reasons for this. On-site water reuse techniques mentioned in this manual require large initial investments, their use requires staff training, and in many cases they also significantly increase the amount of chemicals required for reusing the waste water. On the other hand, the availability of raw water is much less problematic in Finland than in Central Europe. It should be noted that water reuse or recycling as such do not reduce the waste water load at the municipal water and sewage works. Stricter environmental protection requirements have in many countries led companies to complement the waste water treatment technologies with additional recycling systems.

4. Procedures for detergent testing, validation and authorisation

4.1 Authorisation of detergents

Following the standard SFS 3352, all detergent mixtures used in car washing operations must be authorised for this purpose. Upon the manufacturer's or importer's application, the Finnish Petroleum Federation approves all detergent mixtures used for car washing and keeps a central register of all authorised detergent mixtures.

In this manual, a detergent refers to a preparation that is used for washing cars, for instance presoak agents, solvents, shampoos, foam detergents, rinsing agents, waxes and other such chemicals. A detergent mixture, on the other hand, refers to the combination of the above mentioned detergents used in one car wash cycle. Also reused detergents and washbay cleaners are included in the concept of car wash chemicals. In the authorisation procedure, the properties of the detergents are assessed in that composition that they are carried in and delivered to the car wash facility.

If one or more detergents are to be removed from a detergent mixture already authorised, a notification to this effect must be submitted to the Finnish Petroleum Federation. If one or more detergents are to be added to a detergent mixture already authorised, a notification to this effect must be submitted to the Finnish Petroleum Federation. If the detergent mixture that is to be altered contains a petroleum hydrocarbon solvent, even the oil/water separation test must be conducted a second time.

The application must substantiate that the detergent mixture and all of its components meet the approval criteria specified in chapter 4.2. A free-form application with the following attachments is used for seeking the authorisation for a detergent mixture:

- 1) **Safety Data Sheets** (SDS) of all the preparations contained in the detergent. The Decree issued on Safety Data Sheets prescribes that the SDS must be issued in Finnish and/or Swedish, in line with the requirements of the recipient. The contents of the Chemical Notifications submitted in the Chemicals Product Register of the Finnish Safety and Chemicals Agency (Tukes) have been specified in the Decree 553/2008 (amended 965/2011) issued by the Finnish Ministry of Social Affairs and Health.
- 2) **Product Specification** (product formulation). The product Specification must list all the preparations that the detergent contains as well as their approximate percentages. The Product Specifications are handled with the strictest confidentiality, and no data is passed on to third parties.
- 3) **Instructions for use** for all the individual preparations contained in the detergent mixture. Note: All instructions for use issued for detergents for use in Finland must be issued in Finnish and in Swedish.
- 4) **Test Certificate** for the oil/water separation testing issued for the detergent mixture in accordance with Annex 1. No Test Certificate is

required if the detergent mixture contains no detergents that contain a petroleum hydrocarbon solvent.

The oil/water separation testing specified in Annex 1 must be completed by an independent and accredited research institution.

All authorised detergent mixtures are given approval codes and they are registered in the central register of authorised car wash detergents managed by the Finnish Petroleum Federation. The approval code allocated to detergent mixtures that contain petroleum hydrocarbon solvent is "ÖKL xxx", while "ÖKL xxx EL" is the approval code allocated to detergent mixtures that do not contain petroleum hydrocarbon solvents.

The approval code must appear on the packaging of the approved detergent, and the same markings must appear on all the packagings of all the detergents belonging to the detergent mixture in question.

A listing of all detergent mixtures authorised for car wash in Finland is available at the Finnish Petroleum Federation. All detergent authorisations are valid for five years whereupon new applications for approval must be submitted. An updated listing of authorised detergent mixtures is available also on the website of the Finnish Petroleum Federation at www.oil.fi. When a product is removed from the market, the holder of the approval code must notify the Federation to that effect.

4.2 Approval criteria for detergent mixtures

The suitability of a detergent mixture for vehicle wash is tested on the basis of submitted applications. All relevant information concerning the detergent's properties, as well as its occupational health and environmental protection characteristics must be clearly stated in the application. The applicant (manufacturer of the products, their importer or marketer) is responsible for the integrity of the given data and disclosures as well as for the safety of the product.

The detergent mixtures must satisfy the following minimum requirements:

- 1) In the tests described in attachment 1, the total hydrocarbon content (C₅-C₄₀) may in the aqueous phase be 100 mg/l at the very most following an idle period of 45 minutes.
- 2) No detergent in the mixture may be classified as (Decree 807/2001 by the Ministry of Social Affairs and Health):
 - very toxic T+
 - toxic T
 - corrosive C
 - extremely flammable F+
 - highly flammable F
 - dangerous for the environment N¹
 - oxidising O, or
 - explosive E.

These criteria equally apply to detergent concentrates.

¹ Approved are, however, petroleum hydrocarbon solvents that meet the specifications of paragraph 4 of the list when used as presoak agents, even if classified dangerous for the environment.

- 3) The detergent mixture may not contain chlorinated hydrocarbons. The mixture may not contain substances prohibited by the Government decree 1022/2006 (as amended).
- 4) The petroleum hydrocarbon solvent must mainly consist of paraffinic and naphthenic hydrocarbons. The maximum concentration of aromatic hydrocarbons may be 20 percent. The minimum flashpoint of the petroleum hydrocarbon solvent must be 23 C and the maximum density 850 kg/m³.
- 5) No washing chemical contained in the detergent mixture may be harmful for the vehicle surface materials or the car wash bay materials, for instance their paint, rubber or plastic surfaces. Unambiguous instructions must be given on the dosage of the various substances.
- 6) The surface active agents (tensides) contained in the detergent must be aerobically ultimately biodegradable (Detergents Regulation 648/2004/EC). The detergent may not contain nonylphenol ethoxylates.
- 7) The detergent mixture may not contain both a micro emulsion type solvent shampoo and a separate petroleum hydrocarbon solvent.
- 8) The detergent may not contain substances classified as carcinogenic, mutagenic or toxic for reproduction (CMR).

Registrations of substances that may cause cancer carry the following hazard pictograms and R-phrases:

- T - R45 May cause cancer
- T - R45 May cause cancer by inhalation

Mutagenic substances are registered with the following hazard pictogram and

R-phrase:

- T - R46 May cause heritable genetic damage

Substances toxic for reproduction are registered with the following hazard pictograms and R-phrases:

- T - R60 May impair fertility
- T - R61 May cause harm to the unborn child

- 9) The detergent may not contain any nitrilotriacetic acid (NTA) as raw material.

Paragraphs 2 and 8 in the above approval list will be amended as follows on 1 June, 2015 in context with CLP Regulation. If a detergent has been classified before 1 June 2015 based on the amended classification criteria, these criteria will be applied prior to the mentioned date:

- 2) No component of the detergent mixture may be classified under the CLP Regulation as:
- flammable - category 1 and 2
 - acutely toxic - category 1, 2 or 3
 - explosive
 - corrosive to metals - category 1
 - corrosive to the skin - category 1A/1B
 - serious damage to eyes /eye irritation - category 1
 - respiratory sensitizer - category 1
 - dangerous for the environment
 - acute - category 1
 - chronic - category 1 and 2
 - specific target organ toxicant
 - by single exposure - category 1 and 2
 - by repeated exposure - category 1 and 2
 - presenting an aspiration hazard - category 1
 - self-reacting substance or mixture
 - pyrophoric liquid
 - self-heating substance or mixture
 - oxidising liquid
 - organic peroxide.

These criteria equally apply to detergent concentrates.

- 8) Detergent may not contain substances classified as carcinogenic, mutagenic or toxic for reproduction (CMR):
- germ cell mutagen, category 1A or 1B
 - carcinogenic, category 1A or 1B
 - human reproductive toxicant, category 1A or 1B.

4.3 Testing of detergent mixtures

A detergent mixture that contains hydrocarbon solvent and is meant for use in car wash operations must be tested at an independent and accredited laboratory. The test is carried out according to Appendix 1, and it verifies the oil separation qualities of the detergent mixture.

TEST PROCEDURE FOR DETERGENTS CONTAINING HYDROCARBON SOLVENTS

Principle

Testing is always done on the entire detergent mixture. Thereby, the test results indicate their combined effect on the final result. Lubricating oil is added to the mixture in order to make the test mixture better correspond to the composition of the waste water at the vehicle wash facility. The volumes and proportions of the various ingredients of the test mixture correspond to the washing chemical mixing proportions customarily used at automated car washes.

Test mixture

Total volume of the test mixture is 1000 ml. The test is carried out using the following chemicals and quantities:

Hydrocarbon solvent	7,00 ml
Base oil of paraffin based motor oil, viscosity 100...120 cSt/40° C	1,50 ml
Equitable // symmetrical mixture of other washing chemicals	1,00 ml
Distilled water	

Preparation of the emulsion

1. A 1000 ml tap funnel is rinsed twice with pentane and allowed to dry,
2. approximately 700 ml of distilled water is run into the 1000 ml tap funnel,
3. 7,00 ml of hydrocarbon solvent is introduced into the tap funnel with a pipette,
4. 1,50 ml of base oil is introduced into the tap funnel with a pipette,
5. the contents of the tap funnel are mixed by turning it upside down five times,
6. 1,00 ml of a mixture of other washing chemicals is added with a pipette into the tap funnel,
7. distilled water is introduced into the tap funnel until the total volume contained in it is 1000 ml,
8. tap funnel is immediately put into a shaker in which the mixing takes place in longitudinal motions; each stroke is 5 cm in length, the mixing speed is 135 reciprocating strikes per minute, the total mixing time is 60 seconds (timed with a stop watch).

Separation and sampling

- Immediately after the mixing, the tap funnel is placed to a stand avoiding any further mixing.
- After 45 minutes (timed with a stop watch) the first 15 ml of the aqueous layer is drained out through the bottom valve of the tap funnel. After this, a 50 ml water sample is taken into a measuring cylinder for analysis.

Of this sample, its hydrocarbon contents ($C_{10} - C_{40}$) is analysed using the method specified in the standard SFS-EN ISO 9377-2, and its BTEX ($C_5 - C_{10}$) (benzene, toluene, ethyl benzene and xylene) concentration is verified using the method prescribed in the standard SFS-ISO 11423-1. The total hydrocarbon concentration of the sample can be established by adding up these concentrations.

Test certificate

The laboratory that performed the tests issues a Test Certificate for each of the detergent mixtures it tests in line with these guidelines. The certificate declares, at the minimum, the test results, the trade names of all the washing chemicals contained in the tested mixture as well as the name of the entity commissioning the tests.

The detergent mixture is authorised if the hydrocarbon contents of the aqueous phase of the tested mixture ($C_5 - C_{40}$) does not exceed 100 mg/l after the 45 minute idle period.